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SUPPLEMENT TO MELLOR'S COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY

VOLUME II

SUPPLEMENT III

K, Rb, Cs, Fr

A COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY

By J. W. Mellor, D.Sc., F.R.S.

Vol. I.	H, O.
Vol. II.	F, Cl, Br, I, Li, Na, K, Rb, Cs.
Vol. III.	Cu, Ag, Au, Ca, Sr, Ba.
Vol. IV.	Ra and Ac Families, Be, Mg, Zn, Cd, Hg.
Vol. V.	B, Al, Ga, In, Tl, Sc, Ce and Rare Earth Metals, C (Part I).
Vol. VI.	C (Part II), Si, Silicates.
Vol. VII.	Ti, Zr, Hf, Th, Ge, Sn, Pb, Inert Gases.
Vol. VIII.	N, P.
Vol. IX.	As, Sb, Bi, V, Cb, Ta.
Vol. X.	S, Se.
Vol. XI.	Te, Cr, Mo, W.
Vol. XII.	U, Mn, Ma, and Re, Fe (Part I).
Vol. XIII.	Fe (Part II).
Vol. XIV.	Fe (Part III), Co.
Vol. XV.	Ni, Ru, Rh, Pd, Os, Ir.
Vol. XVI.	Pt and general index.

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Suppl.2
pt.3

Supplement to

MELLOR'S COMPREHENSIVE
TREATISE ON

INORGANIC AND THEORETICAL CHEMISTRY

*Prepared under the direction
of an Editorial Board*

VOLUME II

SUPPLEMENT III

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Part 2

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PREFACE

The principles and the methods of selection, assessment and presentation of scientific material employed in the compilation of Supplements to Mellor's "Comprehensive Treatise on Inorganic and Theoretical Chemistry" are now generally familiar to chemists. Moreover they are set out at some length in the prefatory statements which introduced the Supplement on the halogens and that on lithium and sodium (the latter preface mentioning also certain considerations specific to the alkali metals as a group) so that repetition here appears unnecessary. There are, however, two procedures which the Editors consider should be emphasised.

Firstly, it will be evident that contributions share in some measure the individuality of their authors. To a very considerable extent each contributor has exercised his independent judgement concerning the degree of detail in which the various sectors of his review should be treated, and the depth to which new branches of the path of knowledge merit penetration here. The book, like its predecessors in this series of Supplements, is therefore a collection of monographs reflecting, but not precisely conforming with, a common design. Also the scope of the work as described in its general title has not been defined so strictly as to exclude substantial treatment of matters of interest to inorganic and physical chemists in the related fields of organic chemistry, spectroscopy and biology. Further, an attempt has been made to give, wherever possible, precise information rather than to refer to a phenomenon in general qualitative terms, and it has been borne in mind that ideally the source of every statement and its reference in "Chemical Abstracts" should be clearly indicated. That this is not always possible is illustrated by Dr. Heal's explanation that the curves in Figs. 2 to 7 (pages 2538–2543) are largely fictitious, being compiled from various sources of information, but that they represent the bands in their correct positions and with approximately the correct relative heights.

In the second place it is necessary to remind readers that Mellor's convention concerning the location of information about metallic salts continues to be observed. Only the hydrides, oxides, halides, sulphides, sulphates, carbonates, nitrates and phosphates are treated under the general heading of the relevant metal; all other salts are considered under the acids from which they are derived.

It is with deep regret that the Editors record the death of their senior colleague shortly before the completion of the preparation of the material for this Supplement devoted to the chemistry of potassium, rubidium, cæsium, and francium and the radiochemistry of the whole group of alkali metals. By guidance, criticism and example - always for the benefit of "the ordinary chemist" whose needs he identified with his own - Professor H.V.A. Briscoe has contributed notably to the successful launching of the immense task of bringing up to date the comprehensive treatise known familiarly among chemists as "Big Mellor".

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ACKNOWLEDGEMENTS

There is one acknowledgement which is germane to every new Supplement in this series; that is, a tribute to the diligence of many authors, too numerous to specify other than by inclusion in the lists of references, who by means of their presentation, explanation or criticism of experimental results or theoretical views have provided the solid foundation for a comprehensive treatise which essays to review in detail scientific progress over a wide front. The Editors warmly acknowledge the help received from contributors by their ready response to comments or queries and often by their constructive suggestions; the assistance rendered by Mr. N. Adams in reviewing the photoelectric properties of potassium and other alkali metals is also acknowledged with thanks, as is that of Dr. F. Seitz whose publications have notably facilitated the presentation of the section on the effects of ionising radiation on the salts of the alkali metals. They also gratefully acknowledge the encouragement and support that they have received from Governmental and industrial organisations, in particular The Atomic Energy Research Establishment, Harwell, Messrs. Johnson Matthey & Co. Ltd., Imperial Chemical Industries Ltd. (General Chemicals Division) and Scottish Agricultural Industries Ltd., especially in respect of facilities afforded to certain contributors in their survey of published information.

The Editors also express their warm thanks to Messrs. Longmans, Green & Co. Ltd. for the very valuable advice and assistance which are always so freely offered.

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America, published by that Society. Page 1548, fig. 7; page 1551, fig. 9; pages 1791-2, figs. 1-2; page 1917, fig. 14; page 2232, fig. 1; page 2234, fig. 2; pages 2383-7, figs. 2-5; pages 2543-4, figs. 7-8; page 1798, fig. 4 from *Memoirs of the College of Science Kyoto University Series A*, by permission of the Editor. Page 1812, fig. 10 from *National Bureau of Standards Circular 524* published by the U.S. Department of Commerce. Page 1970, fig. 7 from *Nature* published by Macmillan & Co. Ltd. Page 2381, fig. 1 from *Philosophical Magazine* published by Taylor and Francis Ltd. Page 1516, fig. 2; page 1519, fig. 4; page 2154, fig. 2; page 2298, fig. 2; page 2306, fig. 4, from *Physical Review* by permission of the Editor. Page 1518, fig. 3; page 2152, fig. 1; page 2305, fig. 3 from *Proceedings of the Royal Society, Series A*, published by that Society. Page 1970, fig. 8 from *Review of Physical Chemistry of Japan,* published by the Physico-Chemical Society of Japan. Pages 1977-8, figs. 11, 12 from *Soil Science Society of America Proceedings* by permission of the Editor. Page 2217, fig. 1 from *Suomen Kemistilehti* by permission of the Editor. Pages 1597-1602, figs. 1-5; pages 1611-16, figs. 7-13; page 2182, fig. 1 from Smithells, *Metals Reference Book, 2nd. Edition* published by Butterworth Scientific Publications. Page 1749, figs. 5, 6 from *Transactions of the Faraday Society* published by that Society. Page 1610, fig. 6; page 1747, fig. 4; pages 2241-3, figs. 1-5; page 2246, fig. 1; page 2251, fig. 1, 2; page 2395, fig. 2; page 2402, fig. 1; page 2406, fig. 2, from *Zeitschrift für anorganische und allegemaine Chemie* published by Verlag Johann Ambrosius Barth, Leipzig. Page 1980, fig. 13 from *Zeitschrift für Elektrochemie* published by Verlag Chemie GmbH, Weinheim. Page 1527, fig. 6; page 1741, fig. 1; page 1821, fig. 11; page 2313, fig. 6; page 2524, fig. 1; pages 2540-2, figs. 4-6 from *Zeitschrift fur Physik,* published by Springer-Verlag, Heidelberg. Page 2393, fig. 1 from *Zeitschrift für physikalische Chemie* published by Akademische Verlagsgesellschaft, Geest u. Portig K.-G. Leipzig. Page 1802, fig. 5; page 1812, fig. 9 from *Physikalische Zeitschrift* published by Verlag S. Hirzel, Leipzig.

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ABBREVIATIONS

absolute	abs.
alternating current	a.c.
ampère	amp.
Angstrom unit	A.
atmosphere-s (after a numeral)	atm.
atomic weight	at. wt.
boiling point	b.p.
British thermal unit	B.Th.U.
Calorie (large)	kg.-cal.
calorie (small)	g.-cal.
centimetre	cm.
cubic centimetre	c.c.
density (with a numeral)	ρ, d
direct current	d.c.
electromotive force	e.m.f.
foot, feet	ft.
freezing point	f.p.
gram-s (with a numeral)	g.
hour-s (with a numeral)	hr.
inch-es	in.
kilogram	kg.
kilowatt	kW.
litre-s (with a numeral)	l.
melting point	m.p.
milliampère-s	ma.
millilitre-s	ml.
millivolt-s	mV.
minute-s	min.
molecular weight	mol. wt.
parts per million	p.p.m.
potential difference	p.d.
second-s (time only)	sec.
specific gravity	sp. gr.
square centimetre-s	sq. cm.
vapour density	v.d.
vapour pressure	v.p.
volt-s	V.
watt-s	W.
wave-length	λ

LIST OF ADDITIONAL LITERATURE ABBREVIATIONS

For uniformity, the literature abbreviations used in the references are the same as in *An Advanced Treatise on Physical Chemistry* by J.R. Partington, and in Volume 2, Supplements 1 and 2 of this work. In the list which follows, abbreviations are given only for those journals which do not occur in the above sources.

Acta Agral. Fennica. Acta Agralia Fennica. Helsinki, Finland.
Acta Med. Philippina. Acta Medica Philippina. Manila.
Acta Physiol. Acad. Sci. Hung. Acta Physiologica Academiae Scientiarum Hungaricae. Budapest, Hungary.
Agrártudomány. Budapest, Hungary.
Agron. J. Agronomy Journal. Madison, U.S.A.
Amer. Doc. Inst. American Documentation Institute. New York.
Amer. Fertilizer. American Fertilizer. Philadelphia, U.S.A.
Amer. J. Diseases Children. American Journal of Diseases of Children. Chicago, Illinois.
Amer. J. Ophthalmol. American Journal of Ophthalmology. Chicago, Illinois.
Amer. Potato J. American Potato Journal. New Brunswick, U.S.A.
Ann. Botany London. Annals of Botany, London.
Annuar. Regia Staz. Chim. Agrar. Torino. Annuario della Regia Stazione Chimica Agraria in Torino. Turin, Italy.
Arb. Med. Univ. Okayama. Arbeiten aus der Medizinischen Universität Okayama. Japan.
Arb. Staatl. Inst. Exptl. Therap. u. Forsch.-Inst. Chemotherap. Frankfurt. Arbeiten aus dem Staatlichen Institut für Experimentelle Therapie und dem Forschungs-Institut für Chemotherapie zu Frankfurt. Frankfurt, Germany.
Arch. Disease Childhood. Archives of Disease in Childhood. London.
Arch. "E. Maragliano" Patol. e Clin. Archivio "E. Maragliano" di Patologia e Clinica. Genoa, Italy.
Arch. Klin. Chir., Langenbecks. Archiv für Klinische Chirurgie, Langenbecks. Berlin, Germany.
Arch. Inst. Cardiol. Mex. Archivos del Instituto de Cardiologie de Mexico. Mexico.
Arch. Ophthalmol. Graefe's. Archiv für Ophthalmologie vereinigt mit Archiv für Augenheilkunde, Albrecht von Graefe's. Berlin, Germany.
Arch. Phys. Med. Rehabil. Archives of Physical Medicine and Rehabilitation. Chicago, Illinois.
Arch. Sci. Med. Archivio per le Scienze Mediche. Turin, Italy.
Arch. Soc. Biol. Montevideo. Archivos de la Sociedad de Biologia de Montevideo. Montevideo, Uraguay.
Assoc. Southern Agr. Workers. Association of Southern Agricultural Workers. New Orleans, U.S.A.
Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. e Nat. Atti della Accademia Nazionale dei Lincei, Rendiconti, Classe di Scienze Fisische, Matematiche e Naturali. Rome, Italy.
Atti Reale Accad. Lincei. Atti della Reale Accademia dei Lincei. Rome, Italy.

Australian J. Biol. Sci. Australian Journal of Biological Sciences. Victoria.

Beit. Pathol. Anat. u. Allgem. Pathol. Beiträge zur Pathologischen Anatomie und zur Allgemeinen Pathologie. Stuttgart, Germany.

Bergcultures. Indonesia.

Bodas Oro Real Soc. Españ. Fís. y Quím. Crónica Actos Conmem. Conf. Gen. Coloquios y Ses. Cient. Madrid. Bodas de Oro de la Real Sociedad Española de Física y Química. Crónica de los Actos Conmemorativos Conferencias Generales Coloquios y Sesiones Cientificas, Madrid. Spain.

Bodenkultur. Die. Vienna, Austria.

Bol. Inst. Med. Exptl. Estud. Cancer, Buenos Aires. Boletin del Instituto de Medicina Experimental para el Estudio y tratamiento del Cancer, Buenos Aires. South America.

Boll. Tec. Regio Ist. Sper. Colt. Tabacchi "Leonardo Angeloni", Scafati. Bollettino Tecnico del Regio Istituto Sperimentale per la Coltivazione dei Tabacchi "Leonardo Angeloni", Scafati. Rome, Italy.

Bol. Soc. Biol. Santiago Chile. Boletin de la Sociedad de Biologia de Santiago de Chile. Santiago, Chile.

Botan. Arch. Botanisches Archiv.

Botan. Mag. Tokyo. The Botanical Magazine (Tokyo). Tokyo, Japan.

Brit. J. Pharmacol. British Journal of Pharmacology and Chemotherapy. London.

Brown Boveri Rev. The Brown Boveri Review. Baden, Switzerland.

Bull. Naniwa Univ. Bulletin of Naniwa University.

Bull. Orto Botan. Univ. Napoli. Bullettino dell'Orto Botanico della Universita di Napoli. Naples, Italy.

Bull. Sericul. Expt. Sta. Tokyo. Bulletin of the Sericulture Experiment Station, (Tokyo). Tokyo, Japan.

Bull. Tokyo Univ. Forests. Bulletin of Tokyo University Forests. Tokyo, Japan.

Bull. Tulane Univ. Med. Fac. Bulletin of the Tulane University Medical Faculty New Orleans.

Cambr. Phil. Soc. Cambridge Philosophical Society. Cambridge, England.

Canad. J. Med. Technol. Canadian Journal of Medical Technology. Ontario, Canada.

Ceylon Coconut Quart. Ceylon Coconut Quarterly. Ceylon.

Chinese Med. J. Chinese Medical Journal. Peiping, China.

Chromosoma. Berlin, Germany.

Circulation Research. New York.

Compt. Rend. Acad. Agr. France. Comptes Rendus des Séances de l'Académie d'Agriculture de France. France.

Compt. Rend. Soc. Phys. et Hist. Nat. Genève. Compte Rendu des séances de la Société de Physique et d'Histoire Naturelle de Genève. Geneva.

Congr. Intern. Biochim. 2 Congr., Paris, 1952. Congrès International de Biochimie. 2^e Congrès, Paris, 1952. Paris, France.

Debreceni Tisza István Tudományos Társaság II, Osztályának Munkái.

Dermatol. Z. Dermatologische Zeitschrift. Basel, Switzerland.

Deut. Landw. Rundschau. Deutsche Landwirtschaftliche Rundschau. Stuttgart, Germany.

Deut. Lebensm.-Rundschau. Deutsche Lebensmittel-Rundschau. Stuttgart, Germany.

Deut. Tierärztl. Wochschr. Deutsche tierärztliche Wochenschrift-Deutsche tierärztliche Rundschau. Hannover, Germany.

E. African Med. J. East African Medical Journal. Nairobi, Kenya.

El Recien Nacido.

Exptl. Research Sta., Turner's Hill, Cheshunt, Herts., Ann. Rept. Experimental and Research Station, Nursery and Market Garden Industries Development Society Ltd., Turner's Hill, Cheshunt, Herts., Annual Report. Cheshunt, Herts.

Fertilizer Green Book. Atlanta, Georgia.

Fisheries Research Board Canad., Progr. Repts. Pacific Coast Stas. Fisheries Research Board of Canada, Progress Reports of the Pacific Coast Stations. Vancouver, Canada.

Folia Cardiol. Folia Cardiologica. Milan, Italy.

Folia Japon. Pharmacol. Folia Japonica Pharmacologica. Tokyo, Japan.

Forestry Chronicle. Ontario, Canada.

Forschungsdienst. Berlin, Germany.

Gann. Tokyo, Japan.

Gartnertidende.

Giorn. Clin. Med. Parma. Giornale di Clinica Medica (Parma). Parma, Italy.

Glastech. Ber. Glastechnische Berichte. Frankfurt, Germany.

Glutathione, Proc. Symposium Ridgefield, Conn. Glutathione, Proceedings of the Symposium held at Ridgefield, Connecticut. New York.

Hoppe-Seyler's Z. Physiol. Chem. Hoppe-Seyler's Zeitschrift für Physiologische Chemie. Berlin, Germany.

Indian J. Vet. Sci. Indian Journal of Veterinary Science and Animal Husbandry. Delhi, India.

Intern. Congr. Biochem., 1st Congr., Cambridge, Engl., 1949. Abstr. Communs. International Congress of Biochemistry, 1st Congress, Cambridge, England, 1949. Abstracts of Communications. Glasgow, Scotland.

Irish J. Med. Sci. Irish Journal of Medical Science. Dublin, Ireland.

J. Amer. Med. Assoc. Journal of the American Medical Association. Chicago, Illinois.

J. Bath West and Southern Counties Soc. Encour. Agr. Journal of the Bath and West and Southern Counties Society for the Encouragement of Agriculture, Arts, Manufactures and Commerce. Bath, England.

J. Clin. Endocrin. and Metabolism. Journal of Clinical Endocrinology and Metabolism. Springfield, Illinois.

J. Exptl. Botany. Journal of Experimental Botany. London.

J. Fac. Agr., Kyushu Univ. Journal of the Faculty of Agriculture, Kyushu University. Fukuoka, Japan.

J. Histochem. and Cytochem. Journal of Histochemistry and Cytochemistry. Baltimore, Madison.

J. Indian Botan. Soc. Journal of the Indian Botanical Society. Madras, India.

J. Inst. Elec. Engrs. Japan. Journal of the Institute of Electrical Engineers. Tokyo, Japan.

J. Landwirtsch. Journal für Landwirtschaft. Berlin, Germany.

J. Marine Biol. Assoc. United Kingdom. Journal of the Marine Biological Association of the United Kingdom. London.

J. Méd. Bordeaux et Sud-Ouest. Journal de Médecine de Bordeaux et du Sud-Ouest. Bordeaux, France.

J. Ministry Agr. Journal of the Ministry of Agriculture. London.

J. Neurophysiol. Journal of Neurophysiology. Springfield, Illinois and Oxford, England.

J. Physiol. Paris. Journal de Physiologie (Paris). Paris, France.

J. Pomol. Hort. Sci. Journal of Pomology and Horticultural Science. London.

Jahrb. Kinderheilk. Jahrbuch für Kinderheilkunde. Basel, Switzerland.

Jahrb. Wiss. Botan. Jahrbücher für Wissenschaftliche Botanik. Germany.

Keijo J. Med. Keijo Journal of Medicine. Tokyo, Japan.

Landwirtsch. Forsch. Landwirtschaftliche Forschung. Frankfurt, Germany.

Laryngoscope. St. Louis, Missouri.

Len i Konoplya. U.S.S.R.

Lymphatologia Kyoto. Lymphatologia (Kyoto). Kyoto, Japan.

Maataloustieteellinen Aikakauskirja. Helsinki, Finland.

Magyar Biol. Kutatóintézet Munkái. Magyar Biológiai Kutatóintézet Munkái. Budapest, Hungary.

Medd. Centralanstalt. Försöksväsender Jordbruk. Meddelande från Centralanstalten för Försöksväsender på Jordbruksområder. Malmo, Sweden.

Medicine. Baltimore, Madison.

Meldinger Norg. Landbrukshøgskole. Meldinger fra Norges Landbrukshøgskole. Vollebekk, Norway.

Metal Finishing. Westwood, New Jersey, U.S.A.

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CHAPTER 3

POTASSIUM

SECTION XLII

THE OCCURRENCE OF POTASSIUM AND THE EXTRACTION OF POTASSIUM COMPOUNDS FROM NATURAL SOURCES

By P. C. L. THORNE AND K. W. ALLEN

The importance of potassium compounds as fertilizers has caused intensive searches for sources of these compounds during both world wars, when supplies from the usual sources were interrupted. Under these conditions, many poorer sources have been exploited and many processes of extraction worked which would be uneconomical under normal conditions. Such sources and processes are referred to below when they are of sufficient chemical interest.

The production from various sources and estimates of total reserves are commonly given in periodical summaries of mineral production, e.g. U.S. Bureau of Mines publications[1-3] the Annual Review of the World Production and Consumption of Fertilizers (Food and Agriculture Organization of the United Nations) and similar publications.[4-6] The references include a number of surveys over wider periods and dealing with some of the main sites of production.[7-21] It is of interest that the consumption of potash as fertilizer in the United Kingdom during 1953–4 was 250,000 tons of K_2O, ten times the quantity used in 1913.

Potassium is stated to occur in the spectrum of R Andromedae, of R Leonis and of Nova (RS) Ophiuchi. The radioactivity of terrestrial potassium is of importance in the calculation of geological time.[22] The measurements of radioactivity show the emission of 23 β-rays per second, which appears to be a level common to many potassium deposits.[23] More recent work on the age of the earth and of particular deposits uses the ratio of potassium to argon.[24,25] One extensive application of this method to tertiary feldspar from Waldkirch, Germany, gives an estimated age of 223×10^6 years ± 20% in good agreement with estimates by other methods.[26]

The fundamental sources of potassium are igneous rocks. In Nature, the gradual disintegration of these rocks supplies potassium to the soil, whence leaching removes the potassium compounds to rivers, lakes and the oceans. The evaporation of lakes or limbs of seas in geological time has given rise to deposits of salts containing potash which serve as sources of pure compounds and also to augment the natural supplies available in the soil.

The potash-bearing rocks, which are supposed to have been formed late in the crystallization process when water was relatively abundant,[27] are widespread throughout the earth. Those containing leucite have been more intensively investigated with a view to production, for example in Italy[28-31] where the extinct volcano, Rocca Monfina, is estimated to contain 1008×10^6 metric tons of K_2O in a concentration of 21·5%. In Tonkin, between Lao-kai and the Black River, a mixture of eruptive rocks is found to contain potassium,[32] and in Java the Muriah Volcano bears leucite-tephrites with an average content of 5% K_2O.[33] In U.S.A. the shales of Illinois,[34-36] which can be used for making cement, and the greensands of New Jersey[37] are possible sources of potash, though the content ranges only from 2 to 7%. In the greensands the potash is present mainly as glauconite, $KFeSi_2O_6H_2O$. In Sweden an alum shale after the extraction of shale oil gives potash on treatment,[38] and in Finland the ijolite of Iivaara Mountain affords a possible source of potash and other valuable materials.[39] In Poland, Filipowice tuffs from the Cracow region near Kowalska Gora are rich in potassium; one analysis shows 9·68% K_2O.[40]

Poor sources of potassium are concentrated in processes of which the main product is quite different. Thus flue dusts from cement manufacture are collected and lixiviated.[41-46] A great deal of attention has also been paid to the possibility of recovering potassium compounds from blast furnaces. The K_2O content of the charge is low (0·5–0·15%) and not all this appears in the dust collected. The quantity is increased by the addition of common salt or calcium chloride to the charge, when 33–80% of the potassium present is volatilized. The dust is usually precipitated electrostatically and in this way, 5·6 lb. of K_2O are obtained per ton of iron.[47-55] Silicate rocks can also be exploited by fusion with lime[56] or phosphate rock,[57] while the potash in alunite ($Al_2(SO_4)_3 \cdot K_2SO_4, 2Al_2O_3, 6H_2O$) can be similarly extracted from the clay containing it after ignition with[58] or without[59] the addition of limestone. An unusual source of potassium is the tailings of porphyry copper works, which contain 5–10% K_2O.[60]

The occurrence of potassium in soils depends on many complex factors. The actual quantity present is very variable but it is common to find it described as a 'deficiency' in terms of optimum plant needs.[61] Apart from what is artificially added in the form of manures or fertilizers, the potassium in the soil is derived from the disintegration of rocks. Micas are said to be less resistant than felspars,[62-64] and in general an acidic or peaty soil favours the extraction of potassium.[65] Composting the rock with mixtures containing sulphur accelerates the solution of potassium.[66,67] The use of lime or magnesia does not accelerate the decomposition of the rock in the soil.[68,69] On the other hand, potash in the soil is very sensitive to leaching by irrigation or rain[70-73] and is retained only by crystals of certain structures, particularly of the bentonite or montmorillonite types.[74-76] The generally known features of potassium fixation and liberation have been confirmed by a thorough study at the New Jersey Experimental Station, New Brunswick.[77-82]

It is difficult to arrive at a figure for the average content of potash in soils, as the variations are so wide. The results of 1550 analyses of soils in the Palatinate (Germany) by the Neubauer method gave a scale ranging from 'poor' soils with 10 mg. or less to rich soils with over 50 mg. per 100 g.[83,84] The average of thousands of analyses of American soils gave 0·827% K_2O.[85] While the minimum concentration for optimum plant growth ranges from 0·5 to 3·0 p.p.m. depending on the crop,[86] the availability of the potassium depends on the type of soil and especially on the alkalinity.[87-100]

Some springs, lakes and inland seas contain appreciable quantities of potassium, though economic factors may prevent commercial exploitation.[101] In the Dead Sea the total solids are about 20% by weight and of them potassium represents 1·60–1·85%, the total quantity of potassium chloride being estimated at 2000 × 10^6 metric tons.[102,103] At Searles Lake in California potassium chloride is also present in the brine,[104,105] and many other sources are known in U.S.A.; e.g., Nebraska[106] (average 22% K_2O in solids), Great Salt Desert[107] (2·94 g. of potassium per l. of brine), Bay City, Michigan[108] (21·36 g. of potassium per l. of brine), and in the Saratoga Basin.[109] The waste liquors from certain salt works are similar and are used in some areas as a source of potassium. From some Austrian works, concentrations of up to 40 g. per l. of KCL are found,[110] while those from works in the Weser–Saale–Elbe district contain up to 160 g. per l. of mixed chlorides and sulphates of potassium, sodium and magnesium.[111] In the U.S.S.R., potassium is found in the waters of Lake Sacki (KCl, 0·74%),[112,113] in the region of Lake Inder,[114] in and around Lake Dengiz-kul,[115] and in the water of the mud volcanoes in the Caucasus.[116] In Nigeria, Lake Chad has a high potash content and there are other sources of this element.[117,118] Potassium salts have also been found in Sambhar Salt Lake, Rajputana,[119] and in small amounts in Japan.[120,121] It has been pointed out that while in soils plants absorb potassium, in lakes it is adsorbed by silt and in the seas its concentration is reduced by the formation of glauconite.[122]

The potassium chloride content of sea water (0·07%) is found in the mother liquors of the salt obtained by solar evaporation[123,124] and proposals have been made to recover it either in the form of carnallite[125] or as schönite, $K_2SO_4,MgSO_4,6H_2O$.[126-130] More recent suggestions are to treat batches of sea water as a whole with an aromatic nitroamine forming a slightly soluble potassium salt: the separated precipitate is then decomposed with nitric acid and the amine recovered for further use.[131-136]

In view of the theories on the origin of salt deposits, an investigation of one in process of formation in French Somaliland is interesting.[137] The lake is fed from the sea and already one-half is solid salt with rings of gypsum at the edges. The occurrence of potassium as chloride and sulphate at Stassfurt is still one of the most important in the world and controversy still rages as to the origin of these[138-142] and other German deposits, such as those in the Middle Rhine valley[143,144] in Hannover,[145] in Southern Baden[146] and in the Harz.[147,148] After the 1914–18 war, more attention was paid to the deposits of potash in Alsace[149-158] which consist of two layers, 0·80 m. and 0·30 m. thick, separated by 1·80 m. of shale and rock salt.[159] Analyses show a content of potassium chloride ranging from 23·05 to 35·25%, the rest being mainly salt.[160] The annual production from the Alsace mines was stated to be 615,000 tons in 1931 with an expectation that it would rise to 900,000 tons.[161]

The important deposits of Solikamsk (Perm, U.S.S.R.) differ from those of Stassfurt in containing no sulphates but only sodium, potassium and magnesium chlorides, mainly carnallite with less sylvinite, and covered by rock salt.[162-168] The thickness of the carnallite bed ranges from 21 to 100 m. and that of the sylvinite from 12 to 50 m.; prospecting indicates a reserve of K_2O of 6 billion tons under 550 sq. kilometres.[169,170] The sylvinite contains 28–30% KCl, the carnallite 18–20% KCl.

Further surveys have discovered numerous other potassium supplies in the U.S.S.R.[171-173] These are mostly of the same type as the Solikamsk deposits and occur in the Southern Urals,[174] in Central Asia,[175,176] in the Ural-Emba region,[177,178] in Kazakstan,[179] in Ozinskii,[180,181] in the neighbourhood of Lake Inder,[182,183] on the right bank of the Volga[184] and in Prikarpaté (Carpathian Ruthenia).[185]

There are also important minor deposits of potash in other parts of Europe.[186,187] In France,[188-191] in Spain,[192-194] in Poland[195-197] and on Vesuvius[198] potash occurs, but the exploitation of these sources depends on economic factors. In Sicily[199] beds occur with a content of 6·47 to 15·53% K_2O. There are deposits in England in North-east Yorkshire, near Whitby, which have been explored and found to contain polyhalite, kieserite, sylvine and carnallite. They appear to be extensive but are not at present worked because shafts to a depth of 4000 ft. would have to be sunk.[200-202]

In America there are important deposits of Permian age in W. Texas and New Mexico,[203-208] and some potash has been found in Utah.[209,210] In Canada great quantities of mineral containing 35% KCl have been found in beds 435 ft. thick at a depth of 3500 ft.[210,211] at Vera, Saskatchewan. There are indications of deposits in Chile[212] and Peru.[213] Potash deposits at Bahia, Brazil, are interesting as they consist of potassium nitrate, presumably of organic origin.[214] Nitrate deposits also occur extensively in Western Cape Colony and the Transvaal,[215] and this source of potash is the usual one in India.[216] Deposits from a limb of the Red Sea occur in Abyssinia[217] and Eritrea,[218] and beds in Tunis[219] have also been worked.

While the earlier work on the origin of the oceanic salt deposits (see Mellor,II,427) still remains a monument to the application of the phase rule to the study of salt solutions, more recently attention has been given to the geological conditions of formation and to the effects of partial leaching on the original deposits.[138-142,220,221] A recent review[222] summarizes what is now known and gives a select bibliography.

The potash absorbed by plants from the soil can be recovered from the ash of the plant, though this recovery is practised only when the plants are available free of cost or the plant product is a residue from some other process. Seaweeds, especially *Laminaria*, to a total weight of 400,000 tons were collected in Europe each year at the end of the 1914-18 war,[223,234] dried, burned and the ashes lixiviated to yield 10,000 tons of potassium salts. The potassium content of the seaweed is variable, 4–7% in Japanese weeds,[235] while the ash of Australian seaweeds contains on the average 14% of this element.[236] It is important to keep the burning temperature low or potassium chloride may be volatilized.[237,238] The use of seaweeds on the American coasts has also been developed.[239-243] Many marine algae when washed contain more potassium than sodium.[244]

Fresh-water plants are used as sources of potassium only when they grow in great quantities, e.g. the Nile 'sudd'[245] or the water hyacinth of Burma.[246,247] Of land plant sources of potassium the ashes of wood have long been used and it has been calculated that if all the ash of wood burned in the U.S.A. could be collected it would yield over 140,000 tons of K_2O per annum. Actually, the potash available from this source is estimated at 2100 tons of K_2O. The content of K_2O in wood ash varies with the type of wood and ranges from 10% for some softwoods to 35% for hardwoods.[248] The quantity of potash actually obtained falls far short of these maximum figures.[249-251] The refuse from special crops such as sunflowers (in which the K_2O content of the ash may be as high as 37%)[252-254] or hemp,[255] or from weeds, such as ragweeds,[256] moss[257] or bracken,[258] is also used to supply local needs of potash.

Residues from sugar industries, both cane and beet, form an important source of potash, either by burning them directly[259-262] or after the molasses has been fermented for the production of alcohol.[263-276] As an example, a Hawaiian factory obtained 2·5–3·0% of ash containing about 35% K_2O, but in all processes the temperature of combustion must be kept low to prevent the formation of less soluble silicate slags.

The relations between soil potash and plant absorption are not very clear, in spite of much investigation.[277-292] In certain crops definite effects have been observed, e.g. in beet, where halving the K_2O content of the ash had no effect on the sugar content,[293,294] and in tobacco where there is more potash in the better grades;[295] while the application of potash manures to citrus trees was found to result in larger and more numerous fruits, but with decreased sugar content.[296,297] Special qualities in the French wine vintages of 1921 and 1923 were attributed to the potash content; if this is low, insufficient potassium hydrogen tartrate is precipitated.[298-301]

In animals the secretion of potassium has been followed by administration of ^{42}K which can replace 95% of the 40 g. of potassium normally present in the human body.[302,303] Potassium is excreted as sweat – hence the importance of wool washings (which when calcined give an ash containing over 80% of potassium salts),[304] and of wool 'yolks' from which about 30 lb. of potassium salts can be obtained from 1000 lb. of raw wool.[305]

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THE EXTRACTION OF POTASSIUM SALTS FROM NATURAL SOURCES

The general methods of extraction of potassium salts already described (Mellor,II,432,436) have largely remained in use. Subsequent improvements include the use of flotation of the solid crude material in brines of various composition which has been reviewed.[1] In this way the sylvinite ores of Carlsbad can be concentrated to 82–97% KCl using also a sulphated aliphatic alcohol as flotation agent[2] and a 99·9% recovery of potassium chloride is claimed by the use of salts of the primary aliphatic amines, C_{16-18} as flotation agents.[3] Similar treatment of this ore is proposed in the U.S.A.,[4] in the U.S.S.R.,[5] and in France,[6,7] whilst various mechanical methods of separation and their application to potash salts have been reviewed.[8] The use of steam to extract carnallite and crude saltpetre is said to have advantages,[9] as also is the use of reduced pressure and of various devices to speed up the evaporation of the liquors containing the salts in solution,[10] while a method for the electrostatic separation of potash ores has been reported.[11] The Kelly press is recommended for removing slimes from these solutions,[12] though rotary filters and co-current evaporators are sometimes preferred.[13] Mechanical excavation and grinding is necessary not only for the crude material[14,15] but also for the extracted material, as the market is seasonal and the potassium chloride cakes during storage.[16,17]

The addition of phosphate can be used to promote the separation of the potassium in the form of $CaKPO_4$[18,19] or of the magnesium[20] as $MgNH_4PO_4$. Magnesium carbonate can also be used to separate potassium compounds from mixtures; crystals of $MgCO_3,3H_2O$ are formed by the action of carbon dioxide on a dilute suspension of magnesium hydroxide in potassium chloride, and further treatment with carbon dioxide yields a double carbonate: $3(MgCO_3,3H_2O) + 2KCl + CO_2 \rightarrow 2KHMg(CO_3)_2,4H_2O + MgCl_2$. The double salt can be decomposed by heating, cry or in an autoclave, and the potassium carbonate then washed out. Other reactions are possible and strict control of concentrations and temperatures is necessary.[21-23] An alternative way of separating potassium salts is by the use of ammonia and carbon dioxide.[24-26] More recently, treatment of solutions of crude potassium salts with gaseous ammonia and ammonium chloride has been used to precipitate either potassium chloride or sulphate, according to the anions present.[27,28] Carnallite can be leached with mother-liquor from previous operations, which dissolves the magnesium chloride and leaves potassium chloride, or alternatively sulphate liquors may be added and the potassium recovered as the relatively insoluble potassium sulphate.[29,30] The Solikamsk deposits appear to be simpler to work than those of Stassfurt, as the former contain high-grade sylvinite and can be purified as an ideal KCl-$NaCl$-H_2O system, with little interference from calcium sulphate or the small proportion of magnesium chloride present.[31]

The recovery of potassium compounds from brines presents special difficulties. It has, however, been suggested that the underground formation of potash brines by injecting superheated brine deficient in potash may be an economical way of mining thin beds of potash salts.[32,33] If the pH of the brine is raised to 8–10 by adding soda or lime, interference from magnesium and sulphates is eliminated.[34] Solar evaporation is used and the content of sulphate regulated to encourage formation of potassium sulphate under favourable conditions.[35-38] A major problem in the treatment of Searles Lake and Deep Springs brines is the presence of borates – a most undesirable contaminant if the potash is to be used as a fertilizer. Most of the borax can be removed by careful crystallization of the potassium chloride,[39-42] though other methods proposed are precipitation as aluminium borate,[43] hot centrifuging of the moist salts,[44] partial neutralization with acid, followed by concentration and cooling,[45] extraction of boric acid with alcohol[46] and precipitation of the contaminating salts by evaporation under pressure.[47] It may be necessary to precipitate carbonates from some brines either by treatment with lime[48] or with calcium sulphate, which will also remove borates and arsenic.[49] In Japan, precipitation as potassium chlorate or perchlorate is used in treating bittern.[50] The plant for treatment of brines has often had to be specially designed, e.g. continuous plant for crystallization, cooling, evaporation and removal of crystals.[51,52] Potassium can be recovered from dilute solutions such as sea-water by adding a soluble salt of dipicrylamine, when the insoluble potassium dipicrylaminate is precipitated. This can be converted into other salts and the dipicrylamine recovered by treatment with acid.[53-57] The use of synthetic ion-exchange materials has also been reported.[58,59]

In obtaining potash from kelp, the dried weed is now distilled to obtain useful organic products, and the resulting carbonaceous mass is lixiviated to remove potassium salts leaving as a residue a useful decolorizing carbon.[60-64] There have been suggestions for treatment without distillation.[65,66] In a similar way, waste molasses is burnt and the soluble potassium compounds extracted from the ash,[67-79] though dialysis, electrodialysis and ion-exchange have been proposed to extract them without combustion;[80-83] alternatively the potassium may be precipitated as $K_2CaFe(CN)_6$, which on treatment with ferric sulphate yields a solution of potassium sulphate.[84] Potassium salts can also be recovered from the mother liquors of tartaric acid plants, best by direct crystallization as chloride and sulphate.[85] The recovery of potash from wool scourings depends for its economic feasibility on the preliminary recovery of grease by solvent extraction and on operation on a sufficiently large scale.[86-89]

The polyhalite of New Mexico, $K_2SO_4,MgSO_4,2CaSO_4,2H_2O$, is broken down by roasting, either alone or with lime, followed by treatment with limited quantities of water, when either potassium sulphate or K-Mg-schönite is formed.[90-96] In other methods, sodium chloride is added to the extract and potassium chloride is crystallized out;[97-99] or, when lime is used in roasting, syngenite ($K_2SO_4,CaSO_4,H_2O$) may be produced, or ammonium carbonate may be used to precipitate magnesium carbonate,[100-102] or the roasting may be under reducing conditions and give potassium sulphide.[103,104] In a similar way the extraction of potash from alunite can be based on treatment with either hydrochloric acid or an alkali (caustic potash or soda), with or without preliminary roasting.[105-110]

The decomposition of silicates for the separation of potash has been the object of much ingenuity but has often proved unprofitable. The glauconite of greensand is one of the easier silicates to attack, either with acids,[110-113] with lime[114-118] with ferric chloride[119] or with nitrates.[120] The siliceous residue is said to be useful in glass-making or in ceramic materials. More resistant silicates such as wyomingite can be decomposed by heating with lime and a halogen compound so as to volatilize the potassium halide,[121-124] or by the action of nitric acid with oxides of nitrogen,[125] or by extraction under pressure with sodium salt solutions.[126,127] Various other treatments are stated to be effective, and the practicability and economics of known processes have been critically considered, because it is estimated that enough wyomingite is available to supply the potash needed by the U.S.A. for several hundred years.[128]

The extensive deposits of leucite at Rocca Monfina, Italy, contain 10% K_2O and can be exploited in a variety of ways. Dilute sulphuric acid gives potash alum, while dilute hydrochloric acid gives a double potassium aluminium chloride.[129,130] A number of general accounts of the methods used for these deposits have been published,[131-136] but according to Tarchi, only the sulphuric acid treatment is practicable.[137] Among interesting suggestions are treatment with nitrogen oxides, chlorine, acids, alkalis and neutral salts.[138-148] Sometimes the production of mixed fertilizers rather than pure potassium compounds is the object of the treatment, e.g. with phosphates or nitrates.[149-151]

Attempts to obtain potassium compounds from the more refractory silicates in which the element occurs are described in a large number of papers and patents. Treatment with lime or other alkalis is a common method. For example, such minerals are heated with lime and salt to about 1000°C., the potash is leached out and the residue is used as cement;[152,153] in other processes the lime is omitted or replaced by other alkalis.[154-161] When sulphates are required, sodium sulphate is added or the product of heating is leached with sulphuric acid.[162,

[163] Iron and manganese are stated to catalyze the decomposition of the silicate (a process using lime and the chlorides of these metals heated in a stream of air containing hydrochloric acid, is said to extract half the 7–8% K_2O in a felspar);[164] in another similar process 81·7% of the potassium in a felspar was rendered soluble[165] and in yet another the product contained 5·82% of available K_2O;[166] one report denies, however, the usefulness of iron oxide in this extraction.[167] Studies of the mechanism of these reactions suggest that the initial stage is the formation of calcium or sodium oxide, which then reacts with the silica and sets free the potash.[168-170] Alternatively,[171,172] acids or acidic vapours (SO_2, CO_2, HF, HCl, HNO_3) are used at high temperatures.[173-180] Heating strongly, usually in the presence of steam, with calcium cyanide, or calcium cyanamide, or with calcium carbide in nitrogen, is also described as a means of liberating soluble potash from silicates.[181-184] Alunite is used as a source of both potassium sulphate and aluminium oxide, either by leaching with sulphuric acid[185] or by fusion with alkali sulphides.[186] If sodium is present either from the original mineral or from the fusion reagent, the separation of pure potassium salts is more difficult.[186,187]

The volatilization of potassium compounds at high temperatures forms an attractive method of separating them from many contaminants even when the desired element is present only in small amounts. Studies of the relative volatility of potassium compounds important in this connection give the order: KOH, KCl, K_2O from K_2CO_3, K_2SO_4, natural silicates. The actual vapour pressures in mm. of mercury are: KOH (795°), 8; K_2O in K_2CO_3 (970°), 1·68 (1130°), 5·0; K_2SO_4 (1130°), 0·4; KCl (801°), 1·54; (948°), 8·33; (1044°), 34·1 mm. These determinations indicate that the presence of water vapour is advantageous in alkaline mixtures, unless there is enough chloride present to produce the volatile potassium chloride.[188-190] A few proposals have been made to make bricks from special mixtures giving volatile potassium compounds or to smelt such mixtures,[191-195] but far more attention has been given to the recovery of such potash as occurs normally in fumes and dusts from cement kilns and blast furnaces. In cement manufacture, salt of the chlorides of alkaline earth metals may be added to the mix, and sufficient water vapour introduced into the kiln to accelerate the formation of volatile potassium compounds.[196-200] The proportions of lime and silica in the cement mix also affect the volatilization of the potash;[201] using calcium carbonate in the ratio 2CaO:SiO_2, decomposition of the silicate and volatilization of potash begin at about 1150 °C., but with less lime than corresponds with the metasilicate this reaction stops, even at very high temperatures. Added ferric oxide favours the liberation of potassium but added alumina is disadvantageous because it converts the lime into aluminate. The dust is usually collected in flues, sometimes with electrostatic precipitators, and lixiviated to extract the potassium salts.[202-207]

In the recovery of potassium compounds from dusts from blast furnaces it is advantageous to add chlorides to increase the proportion of potash volatilized. The dusts, which are often electrostatically precipitated, contain 20–28% K_2O and this is separated by solution in water and filtration on a rotary filter to yield a product containing 80% of soluble K_2O.[208-215] Attempts have been made, with some success, to volatilize phosphorus simultaneously, using an oxygen-enriched blast.[216] In the absence of chlorides the alkalis tend to form cyanides in the blast furnace, and these on risings are oxidized by the unreduced ores, and are then carried down again by the silica and alumina, to be displaced in turn by calcium to form the permanent slag:[217] this accounts for the observed accumulation of alkali at tuyère level.

Refs. p. 1472

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SECTION XLIII

THE PREPARATION AND USES OF POTASSIUM

By J.P. QUIN

THE PREPARATION OF POTASSIUM IN THE LABORATORY

Since the original Treatise was published some attention appears to have been directed towards the study of methods of formation and preparation of metallic potassium in the laboratory, but it is often found that papers dealing ostensibly with this subject describe work which has in fact been carried out on the preparation of metallic sodium, and then discuss by analogy the production of potassium.

Potassium can be produced by chemical processes which involve thermal decomposition of potassium compounds or reduction of potassium compounds with metallic or non-metallic reducing agents at elevated temperatures, or by electrolysis of potassium compounds in solutions in non-aqueous solvents or in the fused state or electrolytic processes involving the use of an anode consisting of a molten potassium alloy such as potassium amalgam. It is interesting to note that the related metals lithium and sodium which, like potassium, are produced on the commercial scale, are almost invariably prepared by the electrolysis of their compounds, preferably in the fused state, and that chemical methods of preparation are seldom used except in special circumstances. It will be seen, however, that in the case of potassium chemical methods of preparation have been found to offer substantial advantages over the preparation of the metal by electrolysis and have actually superseded electrolytic routes in the manufacture of potassium on the commercial scale.

FORMATION AND PREPARATION OF POTASSIUM BY CHEMICAL REACTION

In general it may be said that chemical reactions analogous to those used in the preparation of sodium (see page 308) are applicable to the preparation of metallic potassium. Many of the methods recommended for the preparation of potassium are advantageously carried out under reduced pressure. However, potassium readily absorbs mercury vapour, even at room temperature, and as the laboratory preparation of potassium is frequently undertaken with a view to obtaining samples of a highly pure metal suitable for determinations of physical or electrical properties of the element, this admittedly small mercury contamination may be very undesirable.[1] In such circumstances it may be preferable to use an oil pump rather than a mercury pump for obtaining the vacuum, or alternatively to make arrangements to avoid contamination of the potassium from back diffusion of the mercury vapour.

Thermal Decomposition of Potassium Compounds.

Potassium is formed by the thermal decomposition of certain potassium salts. Thus, the decomposition of potassium azide in vacuo has been used as a method of preparing small quantities of the metal in the laboratory.[2,3] The decomposition, which is allowed to take place slowly over a period of 3 to 4 days, begins at 355°C. and a steady evolution of nitrogen takes place at

360°C. Under these conditions the liberated metal distils away from the residual mass in the decomposition vessel giving an 80% yield of pure potassium. The light brown residue remaining after the decomposition has taken place reacts with water to give ammonia, thus indicating that some potassium nitride has been formed during the reaction. The method suffers from the disadvantage of being somewhat time consuming owing to the long period necessary for decomposition. Also, as potassium azide tends to be explosive, it is advisable to limit the method to the preparation of small quantities of metal. It is claimed, however, that very pure potassium is obtained, and in particular that the metal is free from hydrogen, and is therefore suitable for work on the determination of physical properties.[2] Potassium is also formed when potassium ferrocyanide or ferricyanide is heated in vacuo[4,5,6] (see page 1480). The formation of potassium, together with potassium cyanide and nitrogen, takes place when potassium cyanamide is heated at 500°C. in an atmosphere of nitrogen. The presence of a mixture of aluminium oxide and ferric oxide accelerates the reaction. Coal also acts as an accelerator.[6a]

The Preparation of Potassium by Thermal Reduction of Potassium Compounds with Metallic and Non-metallic Reducing Agents.

One of the earliest methods for the production of potassium involved the reduction of potassium salts with carbon. Thus, in 1808 Caraudau prepared the metal by reducing potassium carbonate with charcoal at high temperatures, and subsequent workers made a number of improvements in the process. The preparation suffered from the fundamental and serious disadvantage that under certain conditions the potassium and carbon monoxide liberated by the reaction combined to form an explosive compound (Mellor,II,450), and this may help to explain why the development of this route to the metal has been neglected in recent years. However, the reduction of potassium carbonate with carbon:-

$$K_2CO_3 + 2C \rightarrow 2K + 3CO,$$

has been studied,[7] and it was found that potassium monoxide is not produced as an intermediate product during the reduction.

Caradau's work was carried out at normal pressures and at what is described as white heat. It has now been shown that the reduction of potassium compounds with carbon may be advantageously carried out under reduced pressure. Thus, the reaction of an intimate mixture of potassium hydroxide and graphite starts about 700°C. in vacuo, and proceeds readily at 900°C. with a 90% yield of potassium metal.[8]

Potassium is produced when potassium halides are reduced with calcium carbide according to the equation:-[9-11]

$$2KX + CaC_2 \rightarrow CaX_2 + 2C + 2K.$$

When an intimate mixture of 149 parts of potassium chloride and 80 parts of 80% pure calcium carbide is heated to a temperature above the melting point of the potassium salt, preferably in the temperature range 1200–1300°C., metallic potassium is separated by volatilization and condensation.[10] The preparation of potassium may also be carried out by passing potassium chloride vapour, preferably at about 800–1100°C., over solid calcium carbide at a pressure substantially less than atmospheric. Potassium vapour is formed and recovered by condensation.[10a]

Russian workers who have investigated the production of alkali metals by reducing alkali chlorides with calcium carbide have carried out some preliminary experiments on the reduction of potassium chloride.[12] When an intimate mixture of finely ground potassium chloride and calcium carbide is heated at 1000°C. under reduced pressure, potassium metal of good quality is obtained in about 80% yield. The reduction of potassium fluoride with calcium carbide at about 1100°C. under normal pressure forms the basis of a manufacturing process for the production of metallic potassium[13] (see page 1491).

An interesting mode of formation of potassium is the reduction of metallic oxides by potassium cyanide.[14] Metallic oxides, such as lead oxide or nickel oxide, react with potassium cyanide to produce metal from the metallic oxide and also metallic potassium, according to the equation:-

$$2PbO + 2KCN \rightarrow 2Pb + 2CO + N_2 + 2K.$$

The reduction of potassium hydroxide with aluminium takes place in two stages.[15] The primary reaction proceeds according to the equation:-

$$2KOH + Al \rightarrow KAlO_2 + K + H_2.$$

The reduction may be carried out in vacuo at 600°C. and the yield of potassium metal is limited to 50% of the potassium content of the hydroxide owing to the formation of the aluminate. The reaction tends to be violent. In the presence of aluminium, however, potassium aluminate may be reduced at 1350°C. under a pressure of 1·5 mm. of mercury to give potassium. This result was obtained when the reduction was carried out in a porcelain crucible, but when a magnesia crucible was used a mixture of potassium and magnesium metals distilled off at 1300°C. under a pressure of 1 mm. of mercury. A process for the preparation of potassium by the reduction of potassium aluminate with metallic aluminium *in vacuo* has been patented.[15a]

Barium may be used as a reducing agent for potassium compounds.[16] In an ingenious method of preparation, small amounts of potassium are obtained by heating a mixture of potassium chloride and barium azide under reduced pressure. Potassium chloride is added to an aqueous solution of barium azide and the mixture evaporated to dryness in vacuo at room temperature in order to avoid the hydrolysis of barium azide to barium hydroxide which tends to occur at higher temperatures. On heating the mixture to about 100–200°C. the barium azide decomposes to give barium metal which then serves to reduce the potassium chloride to potassium. The reduction may be carried out in glassware at about 400°C. under reduced pressure, and it is stated that under these conditions no distillation of barium takes place. For the preparation of small quantities of potassium this method is said to be better than the reduction of potassium compounds with calcium, magnesium or iron or the direct thermal decomposition of potassium azide.

Beryllium also acts as a reducing agent for the hydroxide.[17] When an intimate mixture of 2 parts of potassium hydroxide and 0·5 parts of beryllium is heated in vacuo at 700°C. the hydroxide is rapidly and completely reduced according to the equation:-

$$2KOH + 2Be \rightarrow 2BeO + 2K + H_2.$$

In a comprehensive survey of laboratory scale methods for the preparation of the alkali metals either by thermal decomposition of alkali salts, or thermal reduction of alkali compounds with metallic or non-metallic reducing agents, Hackspill states that the simplest and most convenient method of preparing potassium is by the reduction of potassium chloride with metallic calcium under reduced pressure.[18] The Hackspill method depends on the reaction of potassium chloride with calcium at about 400°C. under a reduced pressure of preferably 0·01 mm. of mercury, when potassium distils off according to the equation:-

$$2KCl + Ca \rightarrow CaCl_2 + 2K.$$

The reaction may conveniently be carried out in glassware if certain simple precautions are observed, and if the temperature is kept low enough the potassium is obtained in a high degree of purity which is said to compare favourably with that produced by other methods of preparation.[18] At higher temperatures some calcium may distil and contaminate the product, but the potassium can be readily purified by redistillation under reduced pressure.

A number of modifications of the Hackspill method have been proposed.[8,19] Thus, for the preparation of batches of potassium of the order of 100–200 g. it is desirable to use an all-metal apparatus, and one constructed of iron has been described in detail.[8]

Hackspill and his collaborators have made an extensive study of the formation of potassium by the reduction of a number of potassium compounds with iron at elevated temperatures under reduced pressure.[8,15,20] When reduction of potassium chloride, bromide or iodide is attempted with iron in vacuo, the iron halide produced by the reaction tends to volatilize. This volatilized iron halide then reacts in the colder parts of the apparatus with the potassium metal which has distilled over, giving metallic iron and potassium halide, and so reducing the yield of potassium. It is found that when potassium chloride, bromide or iodide is reduced by iron in vacuo at 900–1000°C. the yield of potassium is poor, but rather better results are obtained by using potassium fluoride.[8] When a mixture of potassium nitrate and iron is heated in vacuo at 600°C., potassium is formed according to the equation:-

$$2KNO_3 + 4Fe \rightarrow 2Fe_2O_3 + 2K + N_2.$$

The reaction may be rather violent, and the yield of potassium is poor.[8]

With potassium sulphate the reduction proceeds at about 1000°C. as follows:-

$$2K_2SO_4 + 3Fe \rightarrow Fe_2O_3 + FeS + SO_2 + 3O + 4K;$$

and the yield of potassium is about 80%.[8] Other workers who reduced potassium sulphate with iron in a quartz vessel at a temperature between 875° and 1300°C. obtained a 60% yield of potassium contaminated with considerable amounts of sulphide.[21]

Potassium sulphide may be reduced to potassium by heating it with excess of iron in vacuo at a temperature between 950 and 1000°C. It is suggested that an almost quantitative yield of pure potassium is obtained. This method of preparation is superior to the reduction of potassium sulphate, in that no gaseous products are formed which might contaminate the potassium produced.[8] It is claimed in a patent that potassium may be prepared by the reduction of potassium sulphide with iron, preferably in the presence of an admixed basic oxide or carbonate such as calcium oxide.[22]

The reduction of potassium carbonate with iron, which takes place only with difficulty at 1200°C. under normal pressures, can be carried out at 1000°C. in vacuo according to the equation:-

$$2K_2CO_3 + 2Fe \rightarrow Fe_2O_3 + CO + CO_2 + 4K.$$

The yield of potassium approaches the theoretical, but explosive compounds may be formed by the potassium with the carbon monoxide produced as a by-product.[8]

Potassium cyanide is completely decomposed by iron in vacuo at above 600°C. to give potassium metal in good yield.[8]

The thermal decomposition of potassium ferrocyanide and ferricyanide may be considered to be essentially the reduction of a potassium compound with iron.[4-6,8] Thus, Pinck found that when anhydrous potassium ferrocyanide is heated in a quartz crucible under a pressure of 0·01 to 0·001 mm. of mercury a slight evolution of gas takes place at 300°C.[8] This gas evolution increases with increasing temperature and the composition of the gas changes as follows:-

Temp., °C.	300	300–400	400–450	550
Cyanogen, %	98	60	45	–
Nitrogen, %	–	40	65	98

At 600°C. potassium cyanide volatilizes and at 700°C. potassium metal is formed, leaving a residue of iron and carbon in the crucible. It is suggested that when potassium ferrocyanide, which for this purpose may be regarded as $Fe(CN)_2,4KCN$, is heated in vacuo, the iron cyanide decomposes at about 300°C. as follows:-

$$Fe(CN)_2 \rightarrow Fe + (CN)_2.$$

At 600°C. the reaction is:-

$$Fe(CN)_2 \rightarrow Fe + 2C + N_2.$$

Between these two temperatures the gas evolved is a mixture of cyanogen and nitrogen. At 600°C. the residue remaining after decomposition consists of iron, carbon and potassium cyanide. At 700°C. the potassium cyanide and the iron react to give potassium metal. As the potassium cyanide is present in excess the reaction is incomplete.

Very similar results were obtained by Ormont and Petrov[4,5] who found that when a mixture of potassium ferrocyanide with 50–65% of its weight of iron filings (which are said to catalyze the decomposition) is heated under a pressure of less than 4 mm. of mercury, potassium cyanide is formed at 550–600°C. according to the equation:-

$$K_4Fe(CN)_6 \rightarrow 4KCN + FeC_2 + N_2.$$

The so-called iron carbide is in fact a mixture of iron, graphite and iron carbide. On raising the temperature, the potassium cyanide reacts with the iron and potassium distils off at 850–900°C. It is desirable to cover the reaction mixture with an equal weight of iron filings to prevent distillation of potassium cyanide. It is claimed that very pure potassium is obtained in 80% yield.

The first stage, in which ferrocyanide decomposes to give cyanide, is not influenced by pressure, but it is found that the decomposition of the cyanide does not take place very satisfactorily at pressures greater than about 1 mm. of mercury, and falls off very rapidly at about 100 mm. During the decomposition of the ferrocyanide no ferricyanide is formed.[5]

Potassium is also formed by the thermal decomposition of potassium ferricyanide. This decomposes on heating to give potassium ferrocyanide, which then decomposes in turn in the manner described above.[5]

When potassium thiocyanate is heated with iron in vacuo reduction starts at 500°C. according to the equation:-

$$Fe + KCNS \rightarrow FeS + KCN.$$

On further heating at temperatures above 600°C. in the presence of excess of iron, the potassium cyanide is decomposed to give potassium metal.[8]

Potassium is formed when potassium aluminate is heated with iron in vacuo at about 1550°C., according to the equation:-[15]

$$Fe + 2KAlO_2 \rightarrow Al_2O_3 + FeO + 2K.$$

The maximum yield of potassium that can be obtained when potassium arsenate is reduced with iron in vacuo at 900°C. is about 50%. It is claimed, however, that the metal so produced is highly pure and in particular is free from arsenic.[8]

Small quantities of potassium, together with phosphorus, are formed when potassium metaphosphate is decomposed with iron at 1400°C. in vacuo, according to the equation:-[8]

$$2KPO_3 + 6Fe \rightarrow 6FeO + 2K + 2P.$$

A repetition of the classic experiment of Gay Lussac and Thénard, who prepared potassium by heating metallic iron with potassium hydroxide at a white heat according to the equation:-

$$4KOH + 3Fe \rightarrow Fe_3O_4 + 2H_2 + 4K,$$

has been carried out in vacuo by Pinck. Under these conditions the reduction begins at about 600°C., and at 600–650°C. potassium distils over in 70–80% yield.[8]

Potassium has been prepared by reducing potassium fluoride with magnesium.[13-26] When potassium fluoride is heated with magnesium at 500–700°C.. under a pressure of 11 mm. of mercury., potassium metal distils over at about 540°C. It is claimed that the metal made in this way is of high purity, and the process has been patented.[23-26] Potassium hydroxide reacts explosively with magnesium in vacuo at about 550°C. to form potassium.[8] Potassium is also formed quantitatively when potassium aluminate is heated with magnesium in vacuo at 550°C.[8]

Manganese has been employed as a reducing agent for potassium compounds, and potassium hydroxide can thus be reduced in a current of nitrogen or hydrogen at about 600°C. to yield potassium. The reaction proceeds rapidly at 700°C. When hydrogen is used potassium hydride tends to be formed in preference to the metal.[27]

Attempts to reduce potassium compounds with nickel at high temperatures under reduced pressure have been unsuccessful except in the case of the hydroxide and the sulphide; potassium halides and oxygen-containing salts yield no potassium at temperatures up to 1360°C.[8] When potassium chloride is heated with excess of nickel in vacuo at about 900°C., the chloride distils off unchanged, and the vapour does not react with nickel at temperatures up to 1360°C.[8] Similar results are obtained when a mixture of nickel and potassium iodide is heated in vacuo at temperatures below 1000°C.

Nickel acts as a reducing agent towards potassium hydroxide as iron does, but somewhat less readily.[8] When a mixture of potassium hydroxide and excess nickel is heated under reduced pressure evolution of hydrogen starts at about 500°C. and at about 550–600°C. potassium distils off with some unchanged potassium hydroxide. If the potassium hydroxide vapour is passed through a packed bed of nickel at about 600–650°C., however, it is possible to obtain complete reduction so that potassium alone distils off, leaving a dark brown residue of nickel oxide.

Potassium cyanide does not appear to be reduced by nickel. When mixtures of nickel and potassium cyanide are heated in vacuo at 900°C., much of the cyanide volatilizes and on condensation is frequently found to contain small amounts of potassium. The formation of potassium is attributed, however, not to the reduction of potassium cyanide with nickel, but to the reaction of small amounts of oxide present in the nickel with the cyanide according to the equation:-[8]

$$2NiO + 2KCN \rightarrow 2Ni + 2K + 2CO + N_2.$$

Alternatively, it is suggested that small amounts of potassium hydroxide in the cyanide may be responsible for the formation of potassium metal. If pure nickel and pure potassium cyanide are used, no potassium is formed. When potassium nickel cyanide is heated under similar conditions it decomposes into potassium cyanide, nickel, carbon and gaseous products of composition depending on the temperature.[8] For example, at 350°C. the gas contains 80% of cyanogen and 20% of nitrogen. If the temperature is then raised potassium cyanide volatilizes leaving a residue of metallic nickel.

When potassium thiocyanate is heated with excess of nickel under similar conditions the thiocyanate is decomposed according to the equation:-

$$Ni + KCNS \rightarrow NiS + KCN.$$

At higher temperatures the potassium cyanide then distils off unchanged.[8]

Potassium is also formed when potassium sulphide is reduced with nickel in vacuo at temperatures in the neighbourhood of 1000°C.[8]

Below 1050°C. nickel reacts with potassium sulphate to give potassium oxide, iron sulphide and iron oxide. On further heating at 1350°C. potassium oxide volatilizes but no potassium is formed.[8] The same result is obtained when potassium carbonate is heated with nickel in vacuo at 1360°C.[8]

Although the product of the reduction of potassium hydroxide or chloride with sodium is not pure potassium but a potassium-sodium alloy, it is nevertheless claimed that by combining this reduction with a fractionation of the product, high grade potassium can be obtained.[28] Potassium can also be prepared in this way by the reaction of solid potassium compounds with sodium in the vapour phase.[29]

The manufacture of potassium by the thermal reduction of potassium compounds with sodium is discussed later (see page 1492).

Phosphorus in the form of ferrophosphorus has been used in the preparation of potassium by the reduction of potassium carbonate or hydroxide.[30] According to a patent, ferrophosphorus containing 10–30% or preferably 22–26% of phosphorus is ground to 200 mesh, intimately mixed with potassium carbonate, briquetted, and then heated to 900–1500°C. under reduced pressure, when potassium distils off and may be condensed.[30]

The preparation of potassium by reducing anhydrous potassium compounds, such as the silicate, with silicon or ferrosilicon at 800–1300°C. has also been patented.[31]

Potassium may be prepared conveniently by reducing potassium compounds with zirconium powder at high temperatures under reduced pressure. Zirconium has the advantage of being almost completely nonvolatile under the conditions of the preparation and by selecting suitable potassium compounds it can be ensured that the zirconium compounds formed by the reduction are likewise of low volatility.[21] Thus, potassium chromate and zirconium mixtures in the proportions 1:2 and 1:4 react gently and smoothly to yield potassium. The reaction starts at about 800°C. and a yield of up to 80% of metal free from oxide is obtained.[21]

Mixtures of potassium permanganate and zirconium in the proportions 1:4 react explosively at 300°C., but in the proportion 1:10 the reaction proceeds quietly at the same temperature. In the former case the product is a mixture of potassium with considerable amounts of oxide; in the latter a mixture of about 50% of metal and 25% of oxide is obtained.[21]

When one part of potassium molybdate is heated with 2 parts of zirconium the reaction is explosive, but a 1:4 mixture produces potassium smoothly and gently at 500°C., the yield being about 70%. The product is said to be free from oxide.[21]

With three mixtures of potassium tungstate and zirconium, in the proportions 1:1, 1:2 and 1:4 respectively, potassium is formed smoothly at 570°C.; the yield is about 80% and the product is free from oxide.[21]

Potassium sulphate and zirconium powder in the proportions 1:4 react with explosive violence when heated to about 725°C. under reduced pressure, and the product contains about 20% of potassium metal, together with 20% of oxide and 20% of sulphide and other impurities. With the sulphate and zirconium in the proportions 1:10 reaction is also explosive, but a 50% yield of metal, free from oxide or sulphide, is obtained.[21]

When a mixture of potassium dichromate and zirconium is used in the proportions 1:4 the reduction takes place with explosive violence at 370°C. giving a 40% yield of potassium which, however, is contaminated with about 30% of oxide. With the proportions 1:10, however, the reaction goes smoothly at about 380°C., giving a 40% yield of potassium free from oxide.[21]

The reduction of potassium halides with zirconium is not satisfactory. The zirconium halides formed as by-products of the reaction distil off with the potassium, and in the colder portions of the apparatus the condensed mixture reacts to give metallic zirconium and potassium halide.[21]

Other metallic reducing agents may be used to prepare potassium and the thermal reduction of potassium sulphide with arsenic or tin in a gaseous atmosphere, preferably argon free from oxygen, nitrogen or steam, has been the subject of a patent.[32]

PREPARATION OF POTASSIUM ALLOYS BY CHEMICAL MEANS

Potassium–sodium alloys can readily be obtained by direct combination of the elements.

The most common method is to melt the two metals together under kerosene. This however is not satisfactory, as the alloy tends to divide into small particles coated with dirt. A clean alloy can be prepared by agitating freshly cut sodium and potassium under slightly wet ether.[32a]

Large bright globules of potassium–sodium alloy may be obtained by floating the liquid alloy, previously prepared by melting sodium and potassium under kerosene, in a benzene–ethyl alcohol mixture and adding pieces of clean sodium and potassium till a globule of the desired size is obtained. The alloy so produced is free from dirt.[32b]

When potassium compounds such as potassium hydroxide or the halides react with sodium, reduction is incomplete and a potassium–sodium alloy is produced the composition of which depends on the composition of the fused mixture of potassium and sodium compounds.[33-39c]

Rinck and his collaborators have made a study of equilibria of the type:-

$$KX + Na \rightleftharpoons NaX + K$$

over a wide range of temperature and concentration.[33,33a,34,36-39] The equilibria between potassium and sodium and their hydroxides and halides have been investigated and figures derived for the respective equilibrium constants are shown in Table I.

TABLE I.- EQUILIBRIUM CONSTANTS FOR THE REACTION
$KX + Na \rightleftharpoons NaX + K$

Radical X	Equilibrium Temp.	Equilibrium Constant
Hydroxide	400–700° C.	0·5
Fluoride	1000° C.	0·29
Chloride	800° C.	14·0
Bromide	800° C.	28·9
Iodide	800° C.	56·3

The most favourable reaction for producing potassium is $KF + Na \rightleftharpoons NaF + K$, but it will be seen that in every case the product is not pure potassium but a potassium-sodium alloy of which the potassium content varies according to the concentration of the potassium compound in the fused salt phase at the equilibrium temperature.

A study of this equilibrium by the electrolysis of fused sodium hydroxide-potassium hydroxide mixtures gave rather different values for the equilibrium constant.[40] In the original Treatise (Mellor,II,448) it is stated that potassium can be obtained by melting metallic sodium and potassium hydroxide together in the absence of air, sodium oxide being formed, while potassium distils from the mixture and hydrogen is also evolved. Rinck, however, claims that under the conditions of his experiments the secondary reaction:-

$$Na + NaOH \rightarrow Na_2O + \tfrac{1}{2}H_2,$$

does not take place.[36] Potassium reacts with potassium hydroxide at temperatures above 550°C.,[39] but in a sealed tube and in an atmosphere of hydrogen, evolved by reaction of the alkali metal with the water always present in the hydroxide, this reaction also will not interfere with the equilibrium.[36]

The reaction of potassium compounds such as the hydroxide or the halides can therefore be conveniently employed for the preparation of potassium-sodium alloys. These alloys are also discussed in Chapter II (see pages 316,320).

A patent describes the preparation of a liquid alloy consisting of potassium, sodium and mercury in the atomic ratio 3, 14, and 2 respectively. 23 g. of sodium and 40 g. of potassium are heated under toluene, and the resulting alloy diluted to 1·6 times its volume by the addition of an amalgam produced by adding 11 g. of potassium to 100 g. of 40% sodium amalgam under toluene.[36a] Alloys of potassium with lead or mercury are formed when a lead or mercury salt is treated with a solution of a potassium addition compound of an organic substance such as potassium naphthalene.[36b]

Potassium-sodium-lead alloys have been prepared by the action of metallic sodium on molten potassium chloride[41] or iodide[35] in the presence of molten lead.

ELECTROLYSIS OF SOLUTIONS OF POTASSIUM COMPOUNDS IN NON-AQUEOUS SOLVENTS

The electrolysis of solutions of potassium compounds in non-aqueous solvents might be expected to lend itself to the production of the metal in the laboratory more readily than the electrolysis of fused compounds, which is generally difficult to carry out on a small scale. Direct electrolysis of various non-aqueous solutions of potassium compounds does not appear to be very satisfactory, however, and the best results are obtained with processes which make use of a liquid potassium amalgam anode.[42-46a]

Ewan has patented a process for obtaining potassium by electrolyzing a solution of potassium iodide in liquid ammonia using a copper cathode and a liquid anode consisting of an amalgam containing 0·05% of potassium.[44,45] The electrolysis is carried out at normal pressure, the solution being held at a temperature below its boiling point. The potassium deposited at the cathode dissolves in the liquid ammonia to form a separate liquid phase which is withdrawn and evaporated at normal pressures to give spongy potassium, which is then recast by melting it at as low a temperature as possible and pouring into suitable moulds. It is claimed that by using a dilute solution of potassium iodide the formation of potassium amide is avoided. The cell must be constructed of materials not readily attacked by potassium or ammonia, and ebonite, glass, enamelled iron and copper are recommended.

The preparation of potassium by electrolysis of a solution of potassium amide in liquid ammonia using a potassium amalgam anode has been patented.[46,46a]

According to a patent, potassium can be produced by the electrolysis of a solution containing an anhydrous salt of the metal in anhydrous ammonia and methylamine, ethylamine, or pyridine. The concentration of salt in the electrolyte should be greater than 2 molar, and the resulting potassium can be obtained as a colloid, suspension, paste or deposited metal depending on the salt concentration. The cell should be refrigerated to avoid excessive loss of ammonia at atmospheric pressures.[46b]

The electrolysis of a solution of potassium iodide in anhydrous ethylenediamine, using a potassium amalgam anode, has been recommended as a simple laboratory method for the preparation of potassium in yields varying from 70% to 98%. No experimental details are given, but the preparation of sodium under similar conditions is described.[47]

When solutions of potassium chloride or bromide in nitrobenzene solutions of aluminium chloride or bromide are electrolyzed small amounts of potassium are deposited at the cathode, though when benzene is the solvent no potassium is obtained.[48] Small quantities of potassium have also been prepared by the electrolysis of a solution of potassium iodate in phosphorus oxychloride over several days using a current of 0·01 amp. at 110 V.[50]

The electrolysis of a solution of potassium thiocyanate in pyridine yielded no potassium when a platinum cathode was used, but when a mercury cathode was substituted potassium amalgam was obtained.[51]

More recently however, other workers have succeeded in preparing small amounts of potassium by electrolysis of solutions of potassium iodide, and also potassium thiocyanate, in pyridine. The metal so obtained was amorphous and probably impure.[51a]

The electrolytic deposition of potassium from solutions of potassium salts in liquid sulphur dioxide has been studied.[52,53]

The thiocyanate is one of the few potassium salts easily soluble in liquid sulphur dioxide, and the solution conducts electricity readily. Electrolysis of such solutions with platinum electrodes gives a light coloured deposit at the cathode which darkens on removal from the solvent but does not appear to contain any free potassium.[53] Similarly the electrolysis of solutions of potassium iodide in sulphur dioxide does not yield potassium but unstable potassium compounds.[52] Potassium iodate is only sparingly soluble in sulphur dioxide and the solutions are not good conductors. Electrolysis of such solutions at high voltage over a long period failed to yield any potassium,[53] and a similar result was recorded with potassium chlorate and potassium ferricyanide.[53] The electrolytic deposition of potassium from non-aqueous solutions at normal temperatures has been discussed.[53a-b]

ELECTROLYSIS OF FUSED POTASSIUM COMPOUNDS

Little work has been done on the electrolysis of fused potassium compounds in the laboratory. The Castner process has, however, been applied to potassium by von Hevesy (Mellor,II,448) who electrolyzed potassium hydroxide on a small scale in a modified Castner cell at about 330°C. and obtained potassium metal at about 55% current efficiency.[54,54a]

According to a patent,[55] the secondary reaction which occurs during the electrolysis of fused potassium hydroxide, whereby the liberated hydroxyl ions combine to form oxygen and water with a consequent marked decrease in current efficiency owing to the water reacting with the metal produced by the electrolysis (see also page 336), can be suppressed by the presence of an auxiliary potassium salt able to combine with the hydroxyl ion to reform the compound undergoing electrolysis, with the simultaneous production of gaseous products, such as ammonia, inert towards the molten electrolyte. A suitable auxiliary salt is potassium amide. A similar improvement in current efficiency is obtained when fused potassium nitrate is electrolyzed in the presence of fused potassium carbonate or potassium amide.

According to another patent a similar result may be achieved by carrying out the electrolysis at a temperature not exceeding 450°C. in the presence of 15–42 mol.-% of potassium bromide or iodide.[56] In order to reduce the loss of potassium which results from reaction with water and oxygen at the cathode during the electrolysis of a fused mixture of potassium hydroxide and iodide, it has been proposed to pass a portion of the fused electrolyte continuously into a separate zone, which is heated to a temperature above that of the electrolysis zone, in a counter-current of dry air, thus vaporising dissolved water from the electrolyte before it is recycled for electrolysis.[56a]

A miniature cell designed for the preparation of alkali metals from small amounts of alkali salts has been applied to the preparation of potassium from fused potassium chloride. The electrolysis is carried out in a graphite container which also acts as anode, using an Alundum diaphragm and a stainless steel cathode. The charge consists of about 35–40 g. of potassium chloride, and about 40% of the potassium content of the chloride is readily recovered as metal. Considerably smaller amounts of potassium chloride can be electrolyzed satisfactorily, however, and the method is recommended for obtaining small quantities of the metal from compounds of isotopes of potassium.[57]

Small amounts of potassium have been successfully prepared in the laboratory with a current efficiency of 90–95% by the electrolysis of fused potassium cyanide, which may also contain potassium chloride, using a graphite anode and a nickel cathode with a current of 2·5 amp. at 6 V. Cyanogen is formed at the anode and may be absorbed in potassium hydroxide or carbonate, and the potassium cyanide so formed reutilized in the electrolysis after dehydration.[58]

Potassium has been prepared by the electrolysis of potassium carbonate, in a fused electrolyte containing also a potassium halide, using a graphite or graphitized carbon anode. Electrolysis proceeds satisfactorily with an electrolyte which may contain considerably less than 50% of potassium carbonate, and it is found that even when the potassium carbonate content of the melt falls to 1% or less, no free halogen is liberated at the anode.[59]

Another report states that potassium can be prepared in the pure state by the electrolysis of a mixture of a potassium halide and an oxygen-containing potassium salt, but no details are given.[60] The solubility of potassium in molten potassium chloride, which is important in electrolytic processes, has been discussed[61] (see also page 1550).

A Swedish patent describes the preparation of potassium from an alloy of potassium with tin or a like metal by electrolysis of a fused bath consisting chiefly of potassium borate, the alloy serving as the anode of the cell.[62]

In the electrolysis of fused potassium nitrite, which might be expected to proceed as follows:-

$$KNO_2 \rightarrow K + NO_2,$$

secondary reactions occur and the final products are nitrogen and potassium monoxide at the cathode, and potassium nitrate together with a mixture of nitric oxide and nitrogen dioxide at the anode.[63] The formation of dendrites during the electrolysis of glass has been studied.[63a]

Cathodic processes occurring in the electrolysis of fused potassium chloride, with and without dissolved potassium metal, have been studied.[63b]

Theoretical aspects of the electrolysis of fused potassium salts have also been discussed.[64]

THE PREPARATION OF POTASSIUM ALLOYS BY ELECTROLYSIS

It has been proposed to prepare potassium by the electrolysis of potassium compounds in aqueous solution in the presence of a mercury cathode to form an amalgam from which potassium metal is subsequently recovered by distillation.[42,43]

The preparation of potassium-sodium alloys by the electrolysis of a fused mixture of potassium and sodium hydroxide has been studied[40] using as the cell a rectangular welded iron box, 18 cm. long × 14 cm. wide and 13-14 cm. deep, lined internally with nickel of a minimum thickness of 0·1 mm., and insulated externally with asbestos. The cathode, a pointed rod of nickel or copper, is sealed in an inverted crucible of magnesite or high quality fire-clay dipping into the fused electrolyte with the rim of the crucible 2 cm. above the bottom end of the cathode. The metal and the hydrogen formed at the cathode accumulate in the crucible, which has two holes in the bottom to allow the hydrogen to escape. The anode is a nickel plate, and the cell operates at 45-50 amp. and 9-11 v., with a cathode current density of 10-20 amp./cm.^{2}, and an anode current density not exceeding 0·5-1 amp./cm.^{2} The reversible e.m.f. of the cell was found to be 2·6 v.

Commercial caustic alkali, containing about 2-3% of water and 2-3% of carbonate, is used as raw material, and the mixture of 60% of sodium hydroxide and 40% of potassium hydroxide is dehydrated by heating at 400°C. before starting electrolysis. In the early stages of electrolysis the optimum operating temperature is 220-230°C. but as the electrolyte ages the temperature is raised to 240-260°C. It is not advisable to operate at higher temperatures than 260°C., and in general the lower is the operating temperature the better is the current efficiency. Initially the surface of the electrolyte is clean, but as electrolysis proceeds oxides and carbonates of sodium and potassium accumulate and eventually crystallize out as a crust on the electrolyte surface.

At the same time a carbonate precipitate, which melts only with difficulty, is deposited on the bottom of the cell.

If the removal of the metal phase from the cell is conducted in a skilful manner, however, this surface crust is not harmful. Ladling out of the alloy produced by the electrolysis is carried out every 1–1½ hours. In order to do this the current is switched off the cell and a circular spoon, perforated with small holes, is inserted under the crucible which is then slowly raised so that the metal flows into the spoon. It is found that the electrolyte drains out of the spoon, which retains the liquid alloy. An automatic method of removing the alloy is discussed.

As the duration of the run increases, the composition of the fused hydroxide and metal phase which is formed by the electrolysis undergoes a change. In these circumstances the sodium content of the alloy increases, and this is attributed to the fact that the solid phase impurities precipitated from the electrolyte tend to contain more potassium than sodium.

Normally the process runs quietly and the hydrogen liberated at the cathode burns with a steady flame after ignition. However, an unpleasant feature of the process is the detonation of explosive mixtures which tend to form inside the crucible, especially during the later stages of a run. Ingress of air is the suspected cause, and the detonations constitute a distinct hazard in the immediate vicinity of the cell. With the ageing of the electrolyte iron oxides and silica accumulate in the bath. These substances are reduced to a black mass at the cathode on which they form a lumpy growth. Because of its high resistance, this growth gives rise to severe overheating of the cathode. It is therefore necessary to remove the growth periodically and this is done by heating the cathode to redness when the growth may be stripped off by means of tongs.

The following figures are given for average current yields obtained during prolonged runs:-

Alloy Composition %		Average Current Yield %
Na	K	
60	40	42
50	50	38
40	60	32
25	75	30

Factors influencing current yield are discussed, and dimensions are given for proposed 100 and 200 amp. cells. A cell for the production of potassium-lead alloy by electrolysis of fused potassium chloride in the presence of a molten lead cathode has been described.[64a] The preparation of potassium-lead alloys by dissolving lead in amalgam produced in an electrolytic cell with a mercury cathode, and then removing the mercury by distillation, has been patented.[64b]

Potassium-sodium-lead alloys have been prepared by electrolyzing a fused mixture of sodium and potassium chlorides with a molten lead cathode,[65] and by using fused mixtures of potassium chloride and barium chloride with a cathode of molten tin, antimony or bismuth, alloys of these metals with potassium and barium have been obtained.[66]

Potassium amalgam has been prepared by the electrolysis of aqueous solutions of potassium hydroxide[67] and potassium chloride[68,68a] in the presence of a mercury cathode.

The preparation of potassium amalgam by the electrolysis of aqueous solutions of potassium chloride using a mercury cathode is also discussed in Supplement II, Part I, page 316.

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THE MANUFACTURE OF POTASSIUM

Potassium has but limited uses, and its manufacture has accordingly been restricted to a comparatively small scale. No figures appear to be available for the world production of the metal, but in 1949 the production in the United States was estimated as 25 tons, with an estimated potential production of several thousand tons.[1]

Rather surprisingly, the established method of manufacture of potassium is a thermal process, and not an electrolytic route such as is used in the case of the other common alkali metals sodium and lithium. In this connexion it is interesting to contrast the striking developments which have taken place in the manufacture of sodium from fused sodium chloride in the last thirty years, with what seems an almost complete lack of progress in the production of potassium by electrolysis. Three reasons have been given for the lack of success of electrolyte techniques in potassium manufacture[1a] (a) Potassium has a comparatively high vapour pressure at cell operating conditions, and this gives rise to undesirable metal mist formation in the electrolyte. (b) Corrosion is troublesome at temperatures around the melting point of potassium chloride, and eutectics which would enable electrolysis to be carried out at substantially lower temperatures have not yet been developed. (c) Potassium reacts more easily with oxygen than does sodium, and cell designs, such as the Castner cell, which are satisfactory for sodium, do not provide adequate protection from atmospheric contamination. A possible explanation may also be found in the small tonnages of potassium required for commercial purposes. Most processes using fused electrolyte baths, such as are likely to be applicable to the manufacture of potassium, require a substantial output for efficient operation, whereas thermal processes lend themselves much more readily to the production of comparatively small tonnages.

MANUFACTURE BY CHEMICAL REACTION

The Griesheim Process.

Potassium was manufactured at Griesheim in Germany up to the end of the 1939–45 war when the plant was shut down. It is not known whether manufacture has been restarted.[2] The metal was produced by the thermal reduction of a mixture of potassium fluoride and calcium carbide at normal pressures at a temperature of 1000–1100°C. according to the equation:-

$$2KF + CaC_2 \rightarrow CaF_2 + 2C + 2K.$$

The reduction is carried out in a heat-resisting chromium–nickel steel retort, resembling a large test tube approximately 1 ft. in diameter and 4 ft. long with walls $\frac{1}{4}$ in. thick. The retort is fitted with a removable cover carrying a 2 in. diameter outlet pipe discharging under oil in a receiver. The retort is heated in a coal fired furnace.

The operational procedure is as follows. Dried lump calcium carbide, ground to a fine powder in a ball mill in an inert atmosphere of carbon dioxide and then thoroughly mixed with potassium fluoride, is loaded into the retort and heated to 1000–1100°C. It is not necessary to briquette the mixture. During the heating up period gases evolved from the reaction mixture pass out of the retort via the discharge pipe and bubble through the oil. These gases frequently burst into flame spontaneously as they emerge from the oil and come in contact with the air.

When the evolution of gas ceases and potassium begins to distil over, the old oil receiver is withdrawn and a fresh receiver charged with a clear heavy oil mixture is substituted, so that the progress of the distillation may be watched. The reaction is considered to be finished when no more potassium distils over, and the retort is then allowed to cool. The potassium is then ladled out of the receiver and cast into ingots of a suitable size under oil. When the retort is cool the contents, a mixture of crude calcium fluoride and carbon, are removed and disposed of as waste. The retort is then recharged and the cycle repeated, the total batch time being about three days.

The plant at Griesheim consisted originally of two retorts each producing about 17 kg. of potassium per batch, with a total plant capacity of about 0·8–1·0 metric tons per month. The actual production was about 5–6 metric tons per year. In 1946, however, a newly built plant was available consisting of three furnaces, each retort having an output of 34 kg. of potassium per batch, and the design of the plant was such that three runs per retort could be carried out per day.

Metal made by this process has a potassium content of 99·7–99·8% and contains small quantities of sodium, calcium and magnesium as impurities.

A number of modifications and improvements in this process have been suggested;[2-2b] among them the use of silicon as a reducing agent in place of calcium carbide. This reaction requires the presence of lime to combine with the silica produced by the reduction:-

$$4KF + 4CaO + Si \rightarrow 2CaF_2 + 2CaO,SiO_2 + 4K.$$

The process has the advantage of giving molten end products, whereas the old method did not give a melt at the operating temperature of 1000–1100°C.; moreover, the solidified calcium fluoride–calcium silicate mixture is easily friable, for the melt increases in volume on solidification and crumbles easily because the calcium silicate passes from β- to γ-silicate. This favours easy discharge of the retorts.

The substitution of the comparatively cheap potassium carbonate and silicate for the expensive potassium fluoride has also been investigated. Reduction then proceeds as follows:-

$$2K_2CO_3 + 6CaO + 3Si \rightarrow 3(2CaO,SiO_2) + 2C + 4K$$
$$2K_2SiO_3 + 6CaO + Si \rightarrow 3(2CaO,SiO_2) + 4K.$$

When carbonate is used, the presence of residual moisture in the reactants, particularly in the calcium oxide, may result in the formation of an explosive mixture of gases, and rigorous drying of the raw materials is therefore essential. With potassium silicate, however, the yield is no less and no explosive gas mixtures are formed; moreover, gas evolution in the initial stages of the reaction is much reduced, thus limiting the carry-over of dust particles which clog the outlet tube.

Laboratory tests show that the lime used must contain at least 90% of calcium oxide. The principal impurities present were the oxides of aluminium, iron, magnesium and silicon, and of these alumina is particularly deleterious because it causes the particles of calcium oxide to become encased in a hard semi-sintered shell which hinders the reaction with silica and so reduces the yield of potassium. An excess of about 1·5 times the stoicheiometric amount of calcium oxide is advantageous, as this favours completion of the reaction and also makes the residual waste friable. When silicon is used in place of calcium carbide as the reducing agent, the reactions begin at a lower temperature but require a higher final temperature for completion.

Reduction and Fractional Distillation.

A number of patents describe the manufacture of metallic potassium by the reduction of a potassium compound with sodium, followed by fractionation of the resulting potassium–sodium alloy to obtain pure potassium.[3-6]

What is described as substantially pure potassium may be prepared by the action of sodium on a molten potassium compound at a temperature above the boiling point of potassium but below that of sodium, *i.e.* at 760–880°C., in a vessel provided with a fractionating column. The mixture of sodium and potassium vapour formed by the reaction passes into the column, where cooling at the upper end causes partial condensation that provides a reflux liquid. When the temperature of the uncondensed vapour leaving the column does not exceed 760°C., the product is pure potassium; if, however, the temperature of the escaping vapour rises to 780°C. the product contains about 85% of potassium and 15% of sodium.[4]

Potassium chloride is a cheap potential source of potassium and therefore a very desirable raw material. A process has been patented whereby sodium reacts with molten potassium chloride to yield a mixture of sodium and potassium vapour, which on fractionation gives pure potassium which may then be burned to yield potassium tetroxide. The three stages of the process are combined in a single continuously operating unit with a capacity of 3–5 tons of potassium tetroxide per day, equivalent to approximately 1½–2½ tons of potassium metal per day.[6]

It has been found also that the reduction of a potassium compound, such as potassium chloride or carbonate, may be carried out in the solid state by sodium vapour under reduced pressure, the resultant mixture of potassium and sodium vapour being fractionated as already described. Obviously the reaction temperature must not exceed the melting point of any eutectic mixture that may be formed by the reduction, so that in using potassium chloride the reaction temperature must not exceed 664°C., the melting point of the potassium chloride–sodium chloride eutectic. It is claimed that this process gives a product containing 98–99% of potassium and that the consumption of potassium chloride approaches that required by the equation:-

$$KCl + Na \rightarrow NaCl + K.$$

Other Thermal Processes.

There has been some revival of interest in the use of carbon as a reducing agent for the manufacture of potassium, but there is no evidence that any of the thermal processes described below are operated on a commercial scale.

As was said earlier (see page 1477) the reduction of potassium compounds such as potassium carbonate with carbon suffers from the disadvantage that under certain conditions an explosive potassium carbonyl may be formed by reaction between potassium and the carbon monoxide formed as a by-product of the reduction, and for this or for other reasons the process has become obsolete. Patents have however been granted for a method of producing potassium in which potassium sulphate or chloride is mixed with a non volatile base, such as calcium oxide, and a reducing agent such as coke, and then heated in an induction furnace in an inert atmosphere at a temperature at which the liberated potassium distils off. The metal may then be recovered by condensation.[13]

Reducing potassium hydroxide with carbon at low pressure, Pinck obtained yields of over 90% of potassium at 900°C., and claims that this method is likely to have considerable advantages over the now obsolete industrial method of operation at normal pressures. He points out, however, that the experimental work was carried out on a very small laboratory scale, and that it will be necessary to ascertain that satisfactory yields can be obtained on a technical scale.[8] The preparation of potassium by the reduction of molten potassium hydroxide with carbon at 800–960°C. while a stream of hydrogen or inert gas is passed through the mixture has been patented.[8a]

An apparatus has been patented for the production of alkali metals such as potassium by reducing the carbonate or hydroxide with carbon at low pressure, the potassium vapour being condensed by cooling means placed between the reaction vessel and the pumps.[9,10]

Another method uses as reducing agents carbon or ferrosilicon under a pressure of at least 0·5 atm. at a temperature sufficient to form potassium vapour. The vapour is then expanded to a pressure of 0·4–4·0 mm. mercury and chilled by bringing it in contact with a substantially non-volatile molten metal absorbent, such as lead, from which the potassium is later recovered by distillation. Other quench liquids such as volatile metals miscible with potassium, molten salt mixtures and heavy oils may be used.[11]

In a more recent process, the mixture of potassium vapour and carbon monoxide produced by the reduction of a potassium compound, such as potassium carbonate, with coke is carried forward from the reaction vessel by means of a current of nitrogen and passed up an absorption tower containing molten tin distributed as discrete drops throughout a mass of granular refractory such as silicon carbide. The potassium is desorbed from the tin by a reverse flow of nitrogen.[11a]

A patent describes the preparation of potassium by smelting potassium silicate together with an iron-bearing material such as iron or iron oxide, and a solid carbonaceous reducing material, in an electric furnace. The potassium silicate is reduced to give potassium metal and ferrosilicon. The potassium volatilises and may be suitably condensed.[11b]

MANUFACTURE OF POTASSIUM AND POTASSIUM ALLOYS BY ELECTROLYSIS

Little information is available as to the electrolytic production of potassium on the commercial scale.

An electrolytic process for the manufacture of potassium metal was formerly in operation at Rheinfelden in Germany, but has now been superseded by a thermal route.[2] It was found that when the electrolysis was carried out in a Castner cell using an electrolyte consisting of 66% of potassium hydroxide, 19% of potassium carbonate and 15% of potassium chloride, at about 5 V. and 1100–1200 amp. potassium metal was produced in a continuous manner. An iron cathode and a graphite anode were used. The initial current efficiency was 40% but this gradually fell to about 10%. After a number of trials an electrolyte consisting substantially of potassium chloride and fluoride, with a small percentage of potassium carbonate, was adopted. This electrolyte melted at about 600°C. and the presence of even 1% of potassium carbonate was sufficient to prevent the decomposition of the halogen salts. At a current of 800–900 amp. at 7 V., current efficiencies of over 50% were attained, with an energy efficiency of 100 g. of potassium per kWh.[2a]

Work done in Russia on the production of potassium–sodium alloys with a view to the development of a commercial process has already been described[12] (see page 1487).

A process has been patented for the preparation of potassium from potassium amalgam, which may be prepared by the electrolysis of an aqueous solution of a potassium salt using a mercury cathode, by extraction with liquid ammonia or fused potassium hydroxide to give a solution from which metallic potassium may be subsequently recovered.[12a-b]

There appears to be no record of the manufacture of potassium or potassium alloys by the electrolysis of fused salt mixtures containing potassium chloride in a Downs type cell, using a process analogous to that employed so successfully on the technical scale for the manufacture of sodium. Likewise no evidence has been found that the Ewan process, whereby potassium is made by the electrolysis of a solution of potassium iodide in liquid ammonia using an anode of potassium amalgam, has operated on the commercial scale.

The manufacture of potassium–sodium alloy in a Szechtman cell by electrolysis of a mixture of fused potassium and sodium halides, using a molten lead cathode, followed by distillation of the resultant potassium–sodium–lead alloy to recover potassium–sodium alloy, has been discussed.[12c]

The preparation of potassium amalgam by the electrolysis of aqueous potassium chloride solutions in mercury cathode type cells is discussed in Supplement II, Part I, page 315.

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THE PURIFICATION OF POTASSIUM

Crude potassium contains small amounts of other metals and metallic salts, and also products resulting from interaction with the oxygen, water and carbon dioxide present in the atmosphere. It has been suggested that the purification procedures indicated for sodium may be expected to apply in the case of potassium.[1,1a]

It would appear that metal of a high degree of purity can be obtained by filtration. Potassium or potassium alloys may be purified by a method, attributed to Bunsen, in which the metal, sealed under nitrogen in a glassware vessel containing a sieve, is heated so that it reacts with any moisture, oxygen or carbon dioxide present and is then filtered through the sieve which retains any carbonate or hydroxide.[2] The same principle is applied in the purification of potassium by filtering the molten metal through a small orifice in an evacuated system to remove oxide and other impurities which are insoluble or only partly soluble in liquid potassium.[3]

It is also said that treatment of commercial potassium with controlled amounts of oxygen, followed by filtration at its melting point, will remove

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alkaline earth metals and will also reduce the sodium content of the metal to a low value of <100 p.p.m.[4]

The solubility of potassium monoxide in potassium has been determined and is expressed by wt.-% $O_2 = 0{\cdot}0865 - 0{\cdot}0006089t + 0{\cdot}0000007714t^2$ where t = °C. for the range 65–310°C.

The equilibrium oxide in a potassium–sodium system is exclusively sodium monoxide. The solubility of sodium oxide in potassium and sodium–potassium alloy has been determined and is expressed as wt.-% $O_2 = 0{\cdot}0012 - 0{\cdot}00000871t + 0{\cdot}000000128t^2$ where t = °C. over the range 50–360°C.[4a]

More recent determinations of the solubility of sodium monoxide in potassium–sodium alloys are also available.[4b] The solubility of oxygen in the range 20–176°C. has been determined using apparatus both of glass and of stainless steel.[5] The results give an indication of the extent to which such alloys can be purified by direct filtration. It appears that sedimentation may serve to remove insoluble impurities as a patent describes a method whereby the impure metal is placed in a steel container with an opening at its lower end, and this is then immersed in a molten salt such as potassium chloride, which does not react with potassium. It is claimed that impurities in the potassium sink to the bottom of the tube while purified potassium rises to the top.[6] It has also been proposed to purify potassium by melting it repeatedly in contact with petroleum.[8]

The purification of sodium–potassium alloys by means of cold traps is discussed elsewhere (see page 358).

Potassium has also been purified by solution in non-aqueous solvents followed by filtration. Thus, it has been proposed to purify potassium by dissolving it in liquid ammonia, filtering off the undissolved impurities from the solution, and removing the ammonia by evaporation. No figures are given, however, for the purity of the metal prepared in this manner.[7]

To achieve a final purification of potassium, vacuum distillation of the metal is recommended.[4,9-14] Properly controlled high vacuum distillation of filtered potassium in the temperature range 200–350°C. is said to reduce to negligible proportions such impurities as hydrogen, oxygen, halides, alkaline earth and heavy metals, and to give a significant lowering of the sodium content,[4] but to reduce the sodium content to less than 1 p.p.m. it is necessary to subject the potassium to fractional distillation, or to repeated vacuum distillation in the presence of potassium oxide.[4]

An apparatus for the vacuum distillation of potassium has been described.[9] It is said that when the distillation is carried out in Pyrex glass a highly pure potassium is obtained,[10,13] and that by a triple vacuum distillation the iron content of the metal can be reduced to 0·1 p.p.m.[12]

A combined filtration and vacuum distillation unit for the purification of potassium has been described. Operating data are given.[12a] A sampling device which also serves to separate potassium or potassium–sodium alloys from non-volatile impurities by vacuum distillation has been described. A representative sample of the alkali metal is drawn into a metal foil lined metal receiver, and removed from its impurities directly in the sampler by vacuum distillation.[12a] An apparatus for weighing samples of distilled potassium in an inert atmosphere with high accuracy has been devised.[12c]

A simplified procedure for the simultaneous preparation of several small samples of twice distilled potassium in Pyrex glass ampoules has been described, and it is claimed that commercial potassium can thus be purified to give a product which is free from oxide and other contaminants.[13] Work in which potassium was purified by vacuum distillation in an apparatus constructed of glass containing potassium as the only alkali metal gave potassium having a value for electrical resistance which indicates that it is purer metal than that produced in apparatus made from ordinary Pyrex glass.[14] Other glasses resistant to potassium have been described.[15]

A spectrographic analysis of a sample of sodium–potassium eutectic containing 78 wt.-% of potassium and prepared by the high temperature distillation of a mixture of potassium chloride and sodium showed the following impurities:- Fe 20, Cu 20, Si 20, Al 40, Mg 10, Ca 20 p.p.m. The following elements were not detected: boron, manganese, tin, cadmium, zinc, silver, titanium, zirconium, nickel, cobalt, chromium, lead, bismuth and strontium.[15a]

HANDLING AND STORAGE OF POTASSIUM

Potential hazards associated with the handling and storage of potassium and potassium–sodium alloys have already been discussed and it is only necessary here to mention fire hazards, decontamination of equipment, disposal of potassium-rich residues, and protective clothing for personnel handling potassium.[16-20b]

Sodium and potassium resemble each other very closely, and broadly speaking the precautions outlined in the section dealing with the handling and storage of sodium (see page 362) are equally applicable to potassium. There are, however, minor differences in the properties of the two metals which must be taken into account when dealing with potassium, and these have been discussed in detail by Gilbert.[16] One such difference is that potassium forms an explosive compound with carbon monoxide, whereas sodium carbonyl apparently is not formed at temperatures likely to be used in thermal reduction processes and therefore presents no particular hazard.[16]

The outstanding difference between potassium and sodium, however, probably lies in their oxidation products. Sodium in dry oxygen at ordinary temperatures forms sodium monoxide, and at higher temperatures substantially pure sodium peroxide can be formed. Potassium, however, oxidizes in dry oxygen to potassium tetroxide and this compound can react explosively with metallic potassium.[16] There have been numerous reports of explosions which have occurred while handling potassium, and Gilbert suggests that many of these can be attributed to the formation of potassium tetroxide on the surface of the metal. It is accordingly recommended that potassium should never be allowed to remain in contact with dry air, but should be stored under oil or in an inert atmosphere.[16] Explosions when handling potassium have also been attributed to the reaction of potassium tetroxide, which has formed on the surface of the metal, with the hydrocarbon under which the potassium has been stored.[16b]

The reaction between potassium tetroxide and hydrocarbons such as methyl, ethyl and the higher alcohols, which are frequently used as washing media when cleaning alkali metal systems, may be explosive under certain conditions, and many instances can be cited where violent explosions have resulted from mixing these materials.[18a] While it is true the oxygen is preferentially absorbed by the sodium in a sodium–potassium alloy system, oxidation of the potassium may occur on the walls of tanks or equipment where small amounts of the alloy are not in contact with the bulk of the liquid metal. This oxidation of potassium is also possible on the surface of a layer of molten sodium–potassium alloy, where an oxide layer is formed which prevents direct contact between the alloy and the top of the oxide layer. Under these conditions potassium tetroxide is formed in a sodium–potassium alloy system and in these circumstances an explosive reaction may occur when materials like methyl and other alcohols are used for equipment cleaning. In all cases therefore extreme care must be exercised in the use of alcohols with potassium or sodium–potassium alloys.[18a] (See also page 362).

Potassium is frequently utilized in the form of a potassium–sodium alloy, and the resistance of metallic and non-metallic materials to corrosion by such alloys has been studied over a wide range of temperature. Much of the information given on the resistance of materials to sodium (see page 363) is equally applicable to sodium–potassium alloys. An excellent survey of the available information is given by Miller.[20] Recent engineering experience in handling such alloys at high temperatures indicates that a large number of ordinary metals of construction can be used successfully as containers.[21a] A number of stainless steels have given satisfactory service though with plain carbon steels at high temperature decarburization frequently occurs.

Platinum is severely attacked by potassium–sodium alloys at 600°C.[21] and the use of glass containers is not recommended at temperatures above 250°C.[20] Asbestos may be used as packing for sealing static shafts at temperatures up to 160°C., but not 205°C.[20] Teflon is heavily attacked at 200°C.[21] Ordinary natural or synthetic rubbers disintegrate or lose all flexibility, but some silicone rubbers retain flexibility after a 96-hour exposure to the alloy at 250°C.[22] Graphite is attacked by potassium and its alloys at temperatures above 200°C.[20]

In the United States, potassium–sodium alloys are shipped in stainless steel containers under an inert atmosphere. Standard material can be supplied with oxygen concentrations approaching the solubility of sodium oxide in the alloy at room temperature.[23]

Potassium–sodium alloys stored under purified kerosene will remain in the bright state for several months.[23a]

The preparation of potassium metal dispersions which are stable against settling and agglomeration, and in which the dispersed metal does not exceed 50μ in size, has been described.[24] The preparation of colloidal potassium has been discussed.[17a-c] The information given elsewhere (pages 361 and 362) regarding the handling and application of sodium in the form of dispersions is likely to be equally applicable to potassium.

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THE USES OF POTASSIUM

Potassium can be used for most purposes for which sodium is now employed and indeed is somewhat more reactive than sodium.[1] Sodium, however, is very much cheaper than potassium and consequently the usage of potassium is very severely limited. It is of interest to note that the only use for potassium mentioned in the original Treatise was as a potassium-sodium alloy in high temperature thermometers for use above the boiling point of mercury (Mellor, II, 470). Potassium metal is now used fairly extensively in the form of a sodium-potassium alloy heat transfer fluid.[2-2d] The term 'NaK' has become somewhat widely used to designate such alloys, which are now utilized largely in atomic energy work.[2a] A comprehensive discussion of the problems arising from the use of NaK, with details of the design, construction and operation of liquid metal heat transfer systems using sodium-potassium alloys is given by Trocki.[2]

More recently potassium has been used for the manufacture of potassium tetroxide which can serve as a source of oxygen in gas masks.[3] Metals such as antimony, bismuth, chromium, copper, lead and uranium may be prepared by reducing their oxidized forms with potassium vapour.[4] The production of metals such as titanium, zirconium, beryllium, molybdenum, tungsten and tantalum by reduction of their respective halides in a fluidised process with metallic potassium has been patented.[4a] The preparation of titanium by the reduction of titanium tetrachloride with a potassium-sodium alloy has been patented,[5,6] as has the preparation of metallic powders by reducing a metallic compound with a potassium addition compound of ethers of polyhydric alcohols such as glycol ether,[7] (see page 372). A number of patents cover the refining of metals by treatment with potassium.[7a] Potassium is used as a catalyst for the polymerisation of butadiene in the manufacture of synthetic rubber.[7b]

The amount of potassium used for other purposes is very small indeed. The utilization of the metal in electric lamps and discharge tubes has been

Refs. p. 1500

suggested and methods of introducing the metal into sealed glass tubes have been described.[8-12] Metallic potassium coated with an envelope of soda-lime glass is used as an anode in a primary cell suitable for delivering very small currents.[12a] Lead bearing-alloys containing, among other alloying metals, 1% or less of potassium have been proposed.[13] The use of lead-sodium-potassium alloys containing about .1% of potassium in place of a lead-sodium alloy for the manufacture of tetraethyl lead results in considerably increased yields.[14] Hydrogen, nitrogen and the inert gases may be purified by bubbling them through a liquid potassium-sodium alloy at room temperature in order to remove water and oxygen.[15-15b] Potassium-sodium alloys are also used as a trap for mercury vapour.[16-16c] Miscellaneous proposed uses of sodium-potassium alloys have been discussed.[16a]

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SECTION XLIV

THE PHYSICAL PROPERTIES OF POTASSIUM

By W. H. WILSON

Structure, Atomic and Ionic Radii, Etc.

Hull[1] in his early work (1917) on the crystal structure of the alkali metals was unable to obtain an *X*-ray diffraction pattern with potassium using a powder technique, and it was believed that the metal was completely amorphous. In 1922, McKeehan[2,3] obtained weak reflexions - as from large crystals - when he studied potassium that had been cast in thin-walled glass tubes and cooled to -150°C.; but he reported that the structure did not persist when the temperature was allowed to rise to about 20°C. Contrary to the experience of the earlier workers, Posnjak[4] obtained normal diffraction effects for potassium at room temperature. His results indicated a body-centred cubic lattice with a unit cube dimension, or lattice constant, of 5·333 ± 0·005A. This corresponds to an atomic radius of 2·31A. Other workers[5-7] have since confirmed the body-centred cubic structure at room temperature, and the lattice constant at 20°C. has been given as 5·31A.[6] and 5·32A.[7] The same structure exists at low temperatures:[2,5,8-11] values given for the lattice constant at liquid air temperature include 5·25A.,[5,8] 5·20A.[9] and 5·15A.[2] Goldschmidt[12] in 1926 attributed the absence of a diffraction pattern in room temperature powder photographs for potassium to the existence of single crystals. From Laue photographs he reported a tetragonal structure at ordinary temperatures and it was considered that at low temperatures the single crystals disintegrated into an aggregate of cubic crystals. The tetragonal structure has now, however, been confirmed by later work.[8]

Single crystal rods of potassium have been prepared by allowing the liquid metal to cool very slowly in oiled tubes.[13,14] Andrade and Tsien[14] did this using the same apparatus and technique as was used to prepare sodium single crystal rods (see page 377). Smaller single crystals have been produced by cooling droplets of the liquid metal.[15-17] Well-defined rhombdodecahedra of potassium have been obtained by Neumann and co-workers[15-17] using a special apparatus and the following general procedure. A liquid droplet of potassium, having a diameter of about 1mm. and suspended on a thin silver wire in a high vacuum, was cooled from the bottom to give a single crystal retaining the outer form of the droplet. Then, by condensation of potassium the (110) faces were allowed to build up until a complete rhombdodecahedron was formed. In saturated vapour thin needle crystals of potassium were also found to form. These had a rate of growth about 150 times that for normal potassium crystals. After acquiring a length of 0·5 to 0·8mm. the fast growth stopped and the needles started to thicken.

Barrett[18] cooled specimens of 99·4% potassium to 1·2°K. and then examined them metallographically at 0°C. in a search for a spontaneous martensitic transformation similar to those found at low temperatures with lithium and sodium (see pages 32 and 377). There was, however, no trace of transformation markings on the potassium surfaces. Some slip bands appeared as a result of differential contraction and expansion of the potassium and the glass container, but these were less prominent than in the case of sodium.

Breaks in the plots of electrical resistance and thermoelectric power against temperature were observed by Bidwell[19] in the region of -120°C. (see Fig. 2, page 1516 and Fig. 4, page 1519). These were taken as indicative of a transformation which was thought to be from a crystalline form to an amorphous form.

A preferential crystal orientation giving rise to a fibrous structure has been observed in threads of potassium after thermal and mechanical treatment.[7]

The rate of crystallization of fused, distilled potassium on cooling below its melting point has been studied for various degrees of freedom from oxide.[20] Presence of oxide increases the rate of crystallization.

Glide occurs in single potassium crystals when they are extended slightly, the glide planes being visible as regular and parallel surface markings.[14,21] The spacing of the glide planes is markedly closer at low temperatures than at room temperature. At room temperature the glide plane is (123) and the glide direction [111].

An *X*-ray study of the structure of liquid potassium was made by Thomas and Gingrich[22] over the range 70° to 395°C. Their curves showing the radial distribution of atoms about any one atom in liquid potassium at the two extreme temperatures are reproduced in Fig. 1: the average density curves are included as dotted lines.

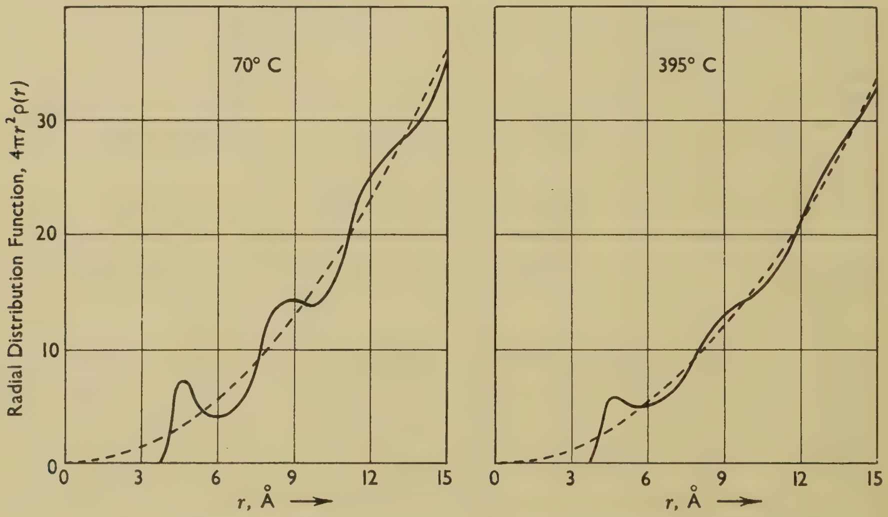

FIG. 1. RADIAL DENSITY DISTRIBUTION OF ATOMS ABOUT ANY ONE ATOM IN LIQUID POTASSIUM AT 70° AND 395°C.

At 70°C., the first peak in the radial distribution curve occurs at 4•64A., and the second peak at about 9•0A., whilst at a temperature of 395°C. the two peaks are shifted to 4•76A. and 9•2A. respectively. At both temperatures, the first peak corresponds to an average concentration of about eight atoms surrounding a given atom. For a few interatomic distances the distribution of atoms about a given atom retains a resemblance to that for the crystalline form, but beyond this region the distribution rapidly becomes random, the randomization setting in at smaller distances for the higher temperature. Lashko[22a] has reported the co-ordination number at 100°C. to be ten, and the distance between atoms 4•7A. At 300°C. the distance between atoms was slightly greater and the co-ordination number dropped to nine. Less detailed studies of the diffraction of *X*-rays by liquid potassium at temperatures just above the melting point have been made by other workers.[23,24] Several theoretical treatments of the structure of liquid potassium have appeared.[25-30a] Hildebrand[27] used the atomic distribution curves of Thomas and Gingrich[22] to calculate the ratio of the energies of vaporization of potassium at 70° and 395°C., while Gingrich and Wall[28] used the same data to calculate the free volume per atom in liquid potassium and, from this, the latent heats of fusion and vaporization. In both cases there was fair agreement with experimentally determined values.

There have been a number of theoretical treatments of the binding and cohesion in metallic potassium.[31-42a] Gorin[31] applied the Wigner-Seitz method (see page 380) and calculated the binding energy and lattice constant of the metal. Agreement between experiment and theory was not as good as in the case of sodium. A statistical model of metals, according to which the metal is composed of a lattice of positive metal ions and a uniformly distributed electron-gas, has been developed by Gombas[32-38a] and used to calculate such quantities as the lattice energy, heat of sublimation, lattice constant, and compressibility of potassium. The lattice energy is taken as the energy of the metal electron gas and the interaction energy between the electron gas and the positive ions; each of these two quantities can be broken down into several component parts and from the final value of the lattice constant the other parameters can be derived in a simple way. Fairly satisfactory agreement with experiment has been achieved.

On the basis of the observed cation–anion distances in NaF, KCl, RbBr, CsI and Li_2O, Pauling[43,44] constructed a set of ionic radii in which the potassium ion was given a radius of 1•33A. Values for the other alkali ions were: Li^+, 0•60A.; Na^+, 0•95A.; Rb^+, 1•48A.; Cs^+, 1•69A. An earlier treatment by Goldschmidt[12] also gave 1•33A. for the radius of the K^+ ion. Detailed accounts of these and other earlier treatments have appeared elsewhere.[44,45]

Density and Thermal Expansion

The density of solid potassium at 18°C. has been reported as[46] 0•8560 and at 20°C. as 0•875.[47] *X*-Ray measurements lead to 0•851 for the room temperature density.[4] Low-temperature measurements have given the density as $0{\cdot}91_5$ at 77°K. and $0{\cdot}92_5$ at 4•2°K.[48] At 100°K. the density calculated from *X*-ray data is 0•89 and the value at 0°K. has been given as 0•90.[5]

From density measurements on liquid potassium between 300° and 600°C., Rinck[49,50] obtained the equation:-

$$d_4^t = 0{\cdot}826 - 0{\cdot}000222(t - 62{\cdot}5)$$

An extrapolation of this line passes exactly through the older value of Hackspill[51] at the melting point, and the equation has been used by Rinck from the melting point up to 800°–900°C. By combining recent American measurements with the older determinations of Hagen[52] and Rinck,[49,50] the values of Table I have been obtained for the density of liquid potassium.[53-55] Other recent density measurements[55a] between the melting point and 735°C. gave a close fit to a straight line; interpolated values at 100°C. and 700°C. were 0•819 and 0•681 respectively.

The increase in volume on fusion has been reported as 2•81%[47] and as

TABLE I.- DENSITY OF LIQUID POTASSIUM

t, °C.	100	200	300	400	500	600	700
g./cm.^{3}	0·819	0·795	0·771	0·747	0·723	0·701	0·676

2·41%[46] or 0·0274 c.c. per gram.

Values for the mean coefficient of linear thermal expansion of potassium over the range 0° to 95°C. for pressures from zero up to 20,000 kg./cm.^{2} are given in Table II.[56,57]

TABLE II.- EFFECT OF PRESSURE ON THE THERMAL EXPANSION OF POTASSIUM

Pressure, kg./cm.^{2}	0	2,000	4,000	6,000	8,000	10,000
α(0 to 95°C.) × 10^5	8·3	$6{\cdot}7_0$	$5{\cdot}3_8$	$4{\cdot}2_7$	$3{\cdot}3_6$	$2{\cdot}6_0$

Pressure, kg./cm.^{2}	12,000	14,000	16,000	18,000	20,000
α(0 to 95°C.) × 10^5	$2{\cdot}2_0$	$1{\cdot}8_3$	$1{\cdot}5_5$	$1{\cdot}3_8$	$1{\cdot}2_5$

Thermal expansion of potassium has been discussed from a quantum mechanical standpoint.[40,58]

Mechanical and Elastic Properties

Bridgman[56,57,59-65] has studied the effect of pressures up to 100,000 kg./cm.^{2} on the volume of potassium. Table III is based on his more recent work.[63,64]

TABLE III.- EFFECT OF PRESSURE ON THE VOLUME OF POTASSIUM AT ROOM TEMPERATURE

Pressure, kg./cm.^{2}	Relative volume	Pressure, kg./cm.^{2}	Relative volume
0	1·000	40,000	0·628
2,500	0·932	50,000	0·595
5,000	0·885	60,000	0·568
10,000	0·814	70,000	0·546
15,000	0·763	80,000	0·528
20,000	0·723	90,000	0·513
25,000	0·691	100,000	0·500
30,000	0·664		

The compressions of the five alkali metals are compared in Fig. 1 (see page 2295). An equation[59] for the volume change at 45°C. for pressures up to 12,000 kg./cm.^{2} needs some revision in the light of later findings.[57,66] A study[48] of the compression of the alkali metals at low temperatures has given the figures in Table IV for the relative volume of potassium at 4·2°K.

TABLE IV.- EFFECT OF PRESSURE ON THE VOLUME OF POTASSIUM AT 4·2°K.

Pressure, atmospheres	Relative volume	Pressure, atmospheres	Relative volume
0	1·000	3,000	0·930
500	0·986	4,000	0·910
1,000	0·972	6,000	0·877
1,500	0·961	8,000	0·848
2,000	0·951	10,000	0·823

At 45°C., Bridgman[59] gave the initial compressibility of potassium as $35{\cdot}6 \times 10^{-12}$ cm.^{2}/dyne. The average compressibility for pressures up to 5×10^8 dynes/cm. at the same temperature was given as $34{\cdot}23 \times 10^{-12}$ cm.^{2}/dyne and that at 20°C. as $32{\cdot}98 \times 10^{-12}$ cm.^{2}/dyne. Recent values[48] for the initial compressibility of potassium at low temperatures are $29{\cdot}2 \times 10^{-12}$ cm.^{2}/dyne at 77°K. and $28{\cdot}4 \times 10^{-12}$ cm.^{2}/dyne at 4·2°K. From measurements[67] of the velocity of ultrasonic waves in liquid potassium (see page 1530), the adiabatic compressibility of liquid potassium at its melting point is $36{\cdot}2 \times 10^{-12}$ cm.^{2}/dyne, and the isothermal compressibility at the same temperature is $40{\cdot}2 \times 10^{-12}$ cm.^{2}/dyne.

Theoretical treatments of the compressibility of potassium have been given by a number of authors.[32-34,36-38,40-42,68-71]

Bender[13] has studied the elastic constants of single potassium crystals at low temperatures. Values at -183°C. were $C_{11} = 0{\cdot}459 \times 10^{11}$, $C_{12} = 0{\cdot}372 \times 10^{11}$, and $C_{44} = 0{\cdot}263 \times 10^{11}$ dynes/cm. The quantum mechanical calculations of Fuchs[72,73] have given the following values for the elastic constants of potassium at absolute zero: $C_{11} = 0{\cdot}45 \times 10^{11}$; $C_{12} = 0{\cdot}38 \times 10^{11}$; $C_{44} = 0{\cdot}26 \times 10^{11}$ dynes/cm.

Surface Properties

Older values of around 400 dynes/cm. for the surface tension of potassium (Mellor,II,456) have been found to be considerably too high. From recent measurements using various experimental techniques it appears that the correct value for the surface tension at the melting point lies within ±10% of 95 dynes/cm. By the maximum bubble pressure method, Taylor[74] obtained 101 dynes/cm. for the value at the melting point; the temperature coefficient was -0·11 dynes/cm./degree. According to Quarterman and Primak,[75] who studied the capillary rise of potassium in glass at temperatures between the melting point and 150°C., the surface tension in the vicinity of the melting point lies between 86 and 95 dynes/cm. Using a drop-weight method, surface tension values between 110 and 150 dynes/cm. have been obtained.[76] These last determinations were considered to be only approximate and there were a number of factors that would be expected to lead to high values. Other measurements[55] have given values of 86 to 80 dynes/cm. for the surface tension of potassium in the range between the melting point and 250°C.

The interfacial tension between potassium crystals and liquid potassium on which no oxide was visible has been given[20] as 0·4 dynes/cm. Higher values are to be expected for potassium completely free from oxide (cf. page 385).

Several theoretical calculations[77-82] of the surface tension of potassium have been made using modern electronic theories, and the resulting values have ranged from[82] 70 to[79] 300 dynes/cm.

Potassium at temperatures between its melting point and 150°C. is reported[75] to wet glass, the contact angle lying somewhere between zero and 26°.

From the surface tension of metallic potassium a value of 140 to 150 is obtained for the parachor. From surface tension data for fused potassium salts the atomic parachor has been calculated[83] to be approximately 110. In aqueous solution the atomic parachor of potassium has been obtained as 110 in salts containing one atom of potassium and 106 in salts containing two atoms of potassium.[84]

Potassium Dispersions and Colloidal Potassium

Dispersions of potassium in many inert liquids with boiling points above the melting point of potassium may be produced by melting potassium under the inert liquid and then agitating vigorously[85] (see page 386).

Molecular condensation methods have been applied to the preparation of colloidal solutions of potassium.[86-90] Metal vapour at a reduced pressure is passed into the cooled dispersion medium, or the mixed vapours of the metal and the dispersion medium may be condensed onto a cooled surface. Potassium sols in ether prepared by such methods have a blue colour and have proved stable for periods of two to three months.[87,88] Electrophoretic measurements have shown the particles to be negatively charged.[88] Potassium iodide is reported to increase the stability and also to increase the migration velocity.[88] Light causes precipitation of metal from the pure sol and precipitation of a blue gel from the protected sol.[88] Potassium sols in benzene, xylene and tripropylamine are reported to be very unstable.[88] Tomashevskii[87] prepared a potassium sol in xylene which had a greenish-blue colour and was stable for ten days. Potassium sols in ethylamine have been found to be stable for 3–5 hours; in this case potassium is also present in true solution.[88]

Ultrasonic waves may also be used to produce colloidal solutions of potassium.[91-92a] Another method that has been described for the preparation of colloidal solutions of alkali metals involves introducing into the dispersion medium a solution of the metal in liquid ammonia and then evaporating the ammonia.[93]

Viscosity

Measurements of the viscosity of potassium have been made up to 200°C. using a glass Ostwald-type viscometer[94] and have been extended to 400°C. using a similar apparatus in nickel.[95] Some of the values are given in Table V.

TABLE V. - VISCOSITY OF POTASSIUM

Temp., °C.	Viscosity, centipoise
69•6	0•514
103•7	0•428
121•5	0•393
147	0•353
167•4	0•329
192•7	0•303
273	0•244
350	0•213

Values up to 200°C. can be represented by the equation:-

$$\eta v^{1/3} = 0{\cdot}9114 \times 10^{-3} e^{742{\cdot}8/vT}$$

and those for the whole range from the melting point to 350°C. by:-

$$\eta v^{1/3} = 0{\cdot}9673 \times 10^{-3}\ e^{716{\cdot}0/vT}$$

where v is the specific volume, T is in degrees Kelvin, and η is in poises. An earlier series of measurements using an oscillating sphere method over the range from the melting point to 350°C.[96] gave results that are in close agreement with the above at low temperatures, but diverge as the temperature increases, and are as much as 14% higher at 350°C. This last work included measurements at temperatures nearer the melting point where the values were 0•5256 centipoise at 67•0°C. and 0•5535 centipoise at 64•2°C. The results up to 350°C. were expressed by the equation:-

$$\eta v^{1/3} = 1{\cdot}293 \times 10^{-3}\ e^{600{\cdot}0/vT}$$

except within a few degrees of the melting point where high values of η suggest the persistence of a crystal structure. More recent measurements[55a] made between the melting point and 735°C., also using an oscillation technique, have given results in accord with the higher values obtained in the previous oscillating sphere measurements. Interpolated values of kinematic viscosity ($\nu = \eta/d$) and viscosities derived from them using the same workers' density values are:-

Temp., °C.	100	200	300	350	400	500	600	700
ν(centistokes)	0•56	0•43	0•36	0•33	0•30	0•27	0•23	0•21
η(centipoise)	0•46	0•34	0•28	0•25	0•23	0•20	0•16	0•14

Other less precise viscosity measurements[97,98] in the vicinity of the melting point are also in close agreement with those given above.

The viscosity of potassium has been related to the binding energy of the molecules of the liquid and to the entropy of bond formation.[99]

Melting Point and Heat of Fusion

A value of 63•20° ± 0•1°C. has been reported for the triple point of pure potassium, and the melting point at atmospheric pressure has been calculated to be 0•02°C. higher than this.[100] Other values for the melting point have included 63•65,[101] 63•35,[102] 62•5,[19,47] and 62•1°C.[46] The variability in the values results, no doubt, from the presence of different amounts of impurity in the samples of potassium used. Extrapolation of freezing point data for sodium–potassium alloys of high potassium content has given 63•7°C. for the melting point of pure potassium.[103] Within the range 92 to 100% potassium the freezing point of a Na–K alloy containing x wt.-% of potassium is given by the equation:-[103]

$$t(°C.) = 63{\cdot}7 - 3{\cdot}86(100 - x)$$

The melting point of potassium increases with increase of pressure and a value of 300°C. has been estimated for the limiting melting point at high pressure.[104] Melting point–pressure curves for the five alkali metals are compared in Fig. 2, page 2298. The potassium curve is from previously quoted determinations of Bridgman (Mellor,II,456). It is seen that the melting point of potassium exceeds that of sodium at pressures above 9000 kg./cm.^{2}

Calorimetric determinations of the heat of fusion of potassium have given 0•568 kg.-cal./g.-atom (equivalent to 14•6 g.-cal./g.)[102] and 59•7 ± 1•2 joule/g. (equivalent to 14•3 g.-cal./g.).[100]

Kelley[105] in 1936 stated that a satisfactory value for the heat of fusion of potassium was not obtainable from any of the then available freezing point data for binary systems involving potassium. The existence in the region near 100% potassium of either a eutectic or two immiscible liquid phases prevents calculation from such data for most binary systems. The systems K–Bi, K–Pb, K–Sb, K–Sn and K–Tl cannot be employed for the first of these reasons and K–Al, K–Cd, K–Li, K–Mg and K–Zn because of the second.

Relationships between the heat of fusion, the variation of melting point with pressure, and the volume change on fusion have been discussed.[104,105a,106,108] A value of 11•5 g.-cal./g. has been obtained for the heat of fusion of potassium from a relationship between the parachor and the heat of fusion.[109]

Vapour Pressure, Boiling Point and Degree of Association

Various methods – both direct and indirect – have been applied to the measurement of the vapour pressure of potassium. Most of the determinations have been carried out at temperatures well below the boiling point. Different types of effusion method have been used in the pressure region below 10^{-2} mm. Hg by Edmondson and Egerton,[101] Mayer[110] and Neumann and Volker.[111] Edmondson and Egerton[101] used Knudsen's effusion method, the rate of flow of potassium vapour through an orifice into high vacuum from a region where the vapour was in equilibrium with liquid potassium at a known temperature being measured by condensing the beam in a cool tube. The resulting deposit was dissolved and its weight determined by chemical analysis. Mayer[110] allowed a similar potassium beam to impinge onto a vane suspended by a quartz fibre, the force exerted by the beam being thereby measured, while Neumann and Völker[111] placed potassium in an evacuated vessel suspended on a torsion fibre and measured the torque when vapour was allowed to escape from two suitably placed holes. Using a static method, Fiock and Rodebush[112] made measurements between 406° and 760°C. over which range the vapour pressure varied from 4·6 to 780 mm.Hg. Measurements of the positive ion current from a tungsten filament in potassium vapour at various temperatures were used by Killian[113] to obtain vapour pressure values, while Weiler[114,115] derived vapour pressures from the magnetic rotation in the vicinity of the first lines of the principal spectral series of potassium. Vapour pressure equations that have resulted from these various measurements are given below; p is in mm. of mercury and T in °K.

Temperature range, °C.	Vapour pressure equation	Authors
100–200	$\log_{10}p = -4507{\cdot}0/T + 7{\cdot}3447$	Edmondson and Egerton[101]
60–140	$\log_{10}p = -4448{\cdot}7/T + 7{\cdot}403$	Mayer[110]
145–199	$\log_{10}p = -4768 \pm 15/T + 11{\cdot}58 \pm 0{\cdot}04 - 1{\cdot}37 \log T$	Neumann and Völker[111]
406–760	$\log_{10}p = -4433/T + 7{\cdot}1830$	Fiock and Rodebush[112]
80–130	$\log_{10}p = -4964/T + 8{\cdot}71$	Killian[113]
155–355	$\log_{10}p = -4375/T + 9{\cdot}866 - \log T$	Weiler[114]
155–297	$\log_{10}p = -4503/T + 10{\cdot}133 - \log T$	Weiler[115]

Several authors[116–119] have reviewed vapour pressure measurements for potassium and have formulated equations embodying the results of two or more sets of workers. Kelley[118] represented the experimental results of a number of workers by the equation:-

$$\log_{10}P(\text{atm.}) = -4769/T + 8{\cdot}708 - 1{\cdot}375 \log T$$

From a graphical analysis of all the previous vapour pressure data for potassium, Ditchburn and Gilmour[119] in 1941 gave the equation:-

$$\log_{10}P(\text{mm.}) = -4552/T + 8{\cdot}793 - 0{\cdot}5 \log T$$

as representing the vapour pressure of potassium within ±5% between 600° and 1100°K. and within ±20% between 350° and 1200°K. Temperatures at which the vapour pressure assumes rounded values as calculated from this last equation[119] are shown in Table VI.

TABLE VI. - VAPOUR PRESSURE OF POTASSIUM

Pressure, mm. Hg	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	760	10^{3}	10^{4}
T, °K. (ref. 119)	364	396	435	482	540	615	716	854	1033	(1060)	(1415)
T, °K. (ref. 120)	(351)	(383)	(422)	(469)	(527)	(603)	704	845	1027	1058	1413

Values in parentheses are extrapolated

Measurements[120] of the vapour pressure of potassium over the range 0·162 to 6·529 atmospheres have been represented by the equation:-

$$\log P(\text{atm.}) = -4207/T + 4{\cdot}096,$$

the standard error in P being 1·1%. Temperatures corresponding to rounded vapour pressures calculated with the aid of this equation are included in Table VI.

From the above vapour pressure measurements[120] extending to pressures of several atmospheres, a boiling point of 1027°K. was obtained. Fiock and Rodebush,[112] who made vapour pressure measurements up to 780 mm.Hg, obtained a value of 1030°K. for the boiling point of potassium. Extrapolations from vapour pressure data obtained at lower temperatures lead to boiling points in the vicinity of the foregoing values. Thus, as seen from Table VI, the vapour pressure equation of Ditchburn and Gilmour[119] gives 1033°K., while the equation of Kelley[118] gives 1047°K.

Evaporation and condensation coefficients of potassium have been studied by Neumann and co-workers.[16,121,122] From microscopic measurements of the decrease in volume of drops of liquid potassium 0·5 to 1 mm. diameter suspended on a thin silver wire in vacuum, the evaporation coefficient was found to have a value of unity and to be independent of temperature over the range 66° to 119°C.[121,122] It was concluded that the potassium atoms evaporate directly into the gaseous phase from each part of the liquid surface. For solid potassium (single crystals) the evaporation coefficient was greater than unity, and increased with decreasing temperature, while the condensation coefficient had a value of approximately unity.[16]

Potassium vapour is essentially monatomic at low pressures. The percentage of diatomic molecules in the vapour increases with increasing pressure, there being present about 5% by volume of such molecules at the normal boiling point. From their spectroscopic measurements,[123,124] Loomis and Nusbaum[123] calculated values of the equilibrium constant for the dissociation of diatomic potassium into atoms for temperatures between 100°C. and the boiling point. Combining them with the vapour pressure data of other workers,[101,112] values calculated for the degree of dissociation (from the equation $K = 4\alpha^2 p/(1-\alpha^2)$) ranged from 0·999878 at 100°C. to 0·9031 at the boiling point. Values for the dissociation constant were calculated by Gordon[125] – also using spectroscopic data – up to higher temperatures (partial pressures are in atmospheres).

T, °K.	298·1	400	600	800	1000
$\log Kp = \log(P_K)^2/P_{K_2}$	−5·247	−2·962	−0·715	+0·420	1·105
T, °K.	1200	1400	1600	1800	2000
$\log Kp = \log(P_K)^2/P_{K_2}$	1·562	1·887	2·129	2·315	2·464

Over the common temperature range, the results are only slightly different from those of Loomis and Nusbaum.[123] The dissociation constants of Gordon[125] when combined with vapour pressure measurements of Fiock and Rodebush[112] lead to the following equation for the vapour pressure of monatomic potassium:-

$$\log_{10} P_K(\text{mm.}) = -4856/T + 11{\cdot}410 - 1{\cdot}275 \log T$$

At the boiling point (1030°K.) the partial pressures of atoms and diatomic molecules in the saturated vapour become 716 mm. and 44 mm. respectively.[125] A more recent calculation[126] of the dissociation constant from spectroscopic data has given values in close agreement with those of Gordon: (partial pressures in atmospheres):-

T, °K.	100	298·16	500	760	1000
$\log Kp = \log(P_K)^2/(P_{K_2})$	−22·89	−5·280	−1·635	+0·234	1·107
T, °K.	1400	1800	2200	2600	3000
$\log Kp = \log(P_K)^2/(P_{K_2})$	1·907	2·356	2·643	2·843	2·990

An experimental study of the dissociation constant of diatomic potassium vapour was made by Lewis[127] over the range 581°K. to 713°K. using a magnetic deflection method. Values for the dissociation constant varied from $\log Kp$ (partial pressures in mm.Hg) = 1·553 at the lowest temperature to $\log Kp$ = 2·566 at the highest temperature (equivalent to −1·328 to −0·315 for partial pressures in atmospheres).

From the slope of the curve of $\log Kp$ against $1/T$, Lewis[127] calculated a value of 15 kg.-cal./g.-mole (≡0·65 e.V.) for the heat of dissociation or dissociation energy of the potassium molecule. He also found this value of the dissociation energy to be that which when put into the Gibson–Heitler formula[128] gave the best representation of his experimental data. An obsolete value of the moment of inertia was, however, used in this last calculation, and Loomis and Nusbaum,[123] using a revised value for the moment of inertia, have calculated the D_0^0 fulfilling the above condition to be 0·56V. Several authors[123,129-133] have derived values for the dissociation energy of the potassium molecule from spectroscopic and other data: the values have ranged from about 0·5 to 0·8 e.V. Hertzberg[134] and Gaydon[135] have listed 0·514 e.V. and 0·51 ± 0·05 e.V. respectively as the best value of the dissociation energy. The U.S. Bureau of Standards selected value[136] for the heat of formation of diatomic potassium vapour is 31·7 kg.-cal./g.-mole at 0°K. and 30·8 kg.-cal./g.-mole at 298·16°K., while the free energy of formation of the gaseous potassium molecule at 298·16°K. is 22·1 kg.-cal./g.-mole.

Heats of Vaporization and Sublimation

Values for the heat of vaporization of potassium at 0°K. calculated from the vapour pressure measurements of various authors lie mostly between 21·6 and 21·8 kg.-cal./g.-mole.[137] Making use of composite data from several sources, Kelley[118] represented the heat of vaporization (to monatomic vapour) by the equation:-

$$\Delta H(\text{kg.-cal./g.-atom}) = 21{\cdot}788 - 2{\cdot}73 \times 10^{-3}T$$

and the free energy of vaporization by:-

$$\Delta F(\text{kg.-cal./g.-atom}) = 21{\cdot}788 + 6{\cdot}29 \times 10^{-3}T\log T - 3{\cdot}997 \times 10^{-2}T$$

For the temperature at which the pressure of potassium atoms becomes one atmosphere (1049°K.), ΔH = 18·924 kg.-cal./g.-atom and ΔS = 18·04 g.-cal./g.-atom.

The U.S. Bureau of Standards selected value[136] for the heat of sublimation of potassium into monatomic vapour is 21·73 kg.-cal./g.-atom at 0°K. and 21·51 kg.-cal./g.-atom at 298·16°K. while the value for the free energy of sublimation is 14·62 kg.-cal./g.-atom at 298·16°K. Kelley[118] has given the following equations for the heat and free energy of sublimation respectively:-

$$\Delta H(\text{kg.-cal./g.-atom}) = 21{\cdot}848 - 0{\cdot}27 \times 10^{-3}T - 2{\cdot}775 \times 10^{-6}T^2$$

$$\Delta F(\text{kg.-cal./g.-atom}) = 21{\cdot}848 + 6{\cdot}2 \times 10^{-4}T\log T + 2{\cdot}775 \times 10^{-6}T^2 - 2{\cdot}655 \times 10^{-2}T$$

These lead to:-

$$\Delta H_{298\cdot1} = 21{\cdot}521 \text{ kg.-cal./g.-atom and}$$
$$\Delta F_{298\cdot1} = 14{\cdot}637 \text{ kg.-cal./g.-atom}$$

Theoretical computations of the heat of sublimation or cohesive energy of potassium have been carried out by a number of authors[32-37,40-42a] (see page 1503).

Specific Heat, Enthalpy and Entropy

Specific Heat.

Simon and Zeidler[138] measured the specific heat of potassium at constant pressure between liquid hydrogen and room temperature. Their potassium contained sodium and lead as impurities, but these amounted to hardly more than 0·1%. A selection of their values for C_p together with values for C_v calculated from them with the aid of the Nernst–Lindemann equation are:-

T, °K.	14·71	19·00	24·21	31·05	41·2	54·0
C_p, g.-cal./g.-atom/deg.	1·23	2·09	2·90	3·75	4·55	5·20
C_v, g.-cal./g.-atom/deg.	1·23	2·09	2·89	3·73	4·51	5·14
T, °K.	71·8	98·3	140·4	201·1	232·1	276·5
C_p, g.-cal./g.-atom/deg.	5·50	5·86	6·17	6·49	6·65	6·90
C_v, g.-cal./g.-atom/deg.	5·41	5·72	5·94	6·13	6·21	6·34

Later measurements[139] on potassium containing less than 0·01% Na have given results in close agreement with the above:-

T, °K.	30	40	60	80	100	150
C_p, g.-cal./g.-atom/deg.	3·70	4·52	5·30	5·70	5·89	6·22
T, °K.	200	250	273·15	298·15	300	330
C_p, g.-cal./g.-atom/deg.	6·46	6·70	6·85	7·07	7·09	7·57

These last results are also in very close agreement with others obtained by Krier, Craig and Wallace[139a] between 12° and 320°K., the average deviation between the two sets of values being only 0·2% above 50°K. and 0·4% below 50°K. Some of Krier, Craig and Wallace's[139a] values are:-

T, °K.	12	14	15	16	18	20	25
C_p, g.-cal./g.-atom/deg.	0·993	1·337	1·508	1·678	2·014	2·345	3·088
T, °K.	30	40	50	60	70	80	100
C_p, g.-cal./g.-atom/deg.	3·681	4·494	4·987	5·307	5·526	5·685	5·890
T, °K.	150	200	250	273·16	298·16	300	320
C_p, g.-cal./g.-atom/deg.	6·213	6·441	6·697	6·840	7·052	7·071	7·348

Measurements[139b] of the specific heat between 1·5° and 20°K. have given the following results:-

T, °K.	1·5	2·0	2·5	3·0	3·5	4·0
C_p, g.-cal./g.-atom/deg.	0·00303	0·0063	0·0120	0·0207	0·0338	0·0513
T, °K.	5	6	7	8	9	10
C_p, g.-cal./g.-atom/deg.	0·103	0·179	0·276	0·389	0·520	0·660
T, °K.	12	14	16	18	20	
C_p, g.-cal./g.-atom/deg.	0·99	1·32	1·65	2·00	2·36	

Carpenter and Steward[102] measured the specific heat of solid and liquid potassium over the range 200° to 600°K.: values for rounded temperatures interpolated from their results are given below:-

T, °K.	200	250	300	336·5(s)	336·5(l)	
C_p, g.-cal./g.-atom/deg.	6·56	6·79	7·36	8·06	8·05	
T, °K.	350	400	450	500	550	600
C_p, g.-cal./g.-atom/deg.	8·00	7·88	7·82	7·80	7·80	7·80

From 250°K. to the melting point they found a large and increasing rise in the specific heat. This rise prior to the melting point, which is characteristic of the alkali metals,[140] has been discussed in terms of lattice deposits.[140a] Other precise measurements[100] of the specific heat of very pure potassium under saturation conditions between 0° and 800°C. have led to the equation:-

$$C_{\text{sat.}} = 0{\cdot}71040 + 2{\cdot}0770 \times 10^{-3}t \ (0° \text{ to } 63{\cdot}2°\text{C.})$$

for solid potassium and to:-

$$C_{\text{sat.}} = 0{\cdot}84074 - 3{\cdot}1688 \times 10^{-4}t + 3{\cdot}1435 \times 10^{-7}t^2 \ (63{\cdot}2° \text{ to } 800°\text{C.})$$

for liquid potassium, $C_{\text{sat.}}$ being in absolute joules/g., and t in °C. The probable errors for these two equations are ±2% and ±0•4% respectively. Table VII shows values obtained from these equations for rounded temperatures.

TABLE VII. - SPECIFIC HEAT, ENTHALPY AND ENTROPY OF POTASSIUM BETWEEN 0° AND 800°C.

Temperature, °C.	$C_{\text{sat.}}$ g.-cal./g.-atom/deg.	$H_t - H_{0°\text{C.}}$ g.-cal./g.-atom	$S_t - S_{0°\text{C.}}$ g.-cal./g.-atom/deg.
0	6•639	0	0
25	7•124	172	0•602
50	7•609	356•2	1•195
63•2(s)	7•866	458•3	1•505
63•2(l)	7•681	1016	3•163
75	7•651	1106	3•427
100	7•590	1297	3•956
200	7•382	2045	5•732
300	7•233	2775	7•133
400	7•142	3494	8•289
500	7•111	4206	9•275
600	7•138	4918	10•141
700	7•223	5636	10•919
800	7•368	6365	11•632

Above the melting point the specific heat falls with rise of temperature to a minimum value at about 500°C. These last measurements gave values for liquid potassium several percent lower than the earlier measurements of Carpenter and Steward[102] which are considered[100] to be less precise. Other less precise values for the specific heat of liquid potassium at 90°, 136° and 181°C. have been obtained by measuring the adiabatic temperature-pressure coefficient.[141] In reviewing thermal data up to 1948, Kelley[142] gave the following equation as representing within ±1% the specific heat of solid potassium between 298°K. and the melting point:-

$$C_p = 6{\cdot}04 + 3{\cdot}12 \times 10^{-3}T \ (C_p \text{ in g.-cal./g.-atom, } T \text{ in °K.})$$

Values selected for the heat capacity of solid and liquid potassium in a recent survey[137] of the thermodynamic properties of the alkali metals are shown in Table VIII.

From the vibration frequency, Kelley[142] represented the heat capacity of diatomic potassium vapour by the equation:-

$$C_p = 8{\cdot}94 - 0{\cdot}03 \times 10^5 T^{-2}$$

(accuracy ±0•5% between 298° and 2000°K.; C_p in g.-cal./g.-mole; T in °K.) Values,[126] calculated from spectroscopic data, for the heat capacity of both monatomic and diatomic potassium vapour at one atmosphere pressure are

TABLE VIII. - THERMODYNAMIC FUNCTIONS FOR SOLID AND LIQUID POTASSIUM BETWEEN 0° AND 1000°K.

Temp., °K.	C_p° g.-cal./g.-atom/deg.	$(H_T^\circ - H_0^\circ)/T$ g.-cal./g.-atom/deg.	S_T° g.-cal./g.-atom/deg.	$-(F_T^\circ - H_0^\circ)/T$ g.-cal./g.-atom/deg.
0	0	0	0	0
50	4·99	2·654	4·426	1·772
100	5·94	4·118	8·259	4·141
150	6·28	4·788	10·739	5·951
200	6·50	5·189	12·576	7·387
250	6·71	5·471	14·048	8·577
273·16	6·88	5·583	14·649	9·066
298·16	7·16	5·703	15·262	9·559
300	7·18	5·711	15·306	9·595
336·4(sol.)	7·91	5·909	16·169	10·260
336·4(liq.)	7·68	7·556	17·816	10·260
400	7·53	7·561	19·130	11·569
500	7·34	7·534	20·789	13·255
600	7·20	7·489	22·114	14·625
700	7·13	7·442	23·218	15·776
800	7·11	7·401	24·168	16·767
900	7·16	7·371	25·008	17·637
1000	7·26	7·354	25·767	18·413

shown in Table IX. Other recent calculations[137] have given values in close agreement with those of Table IX (see page 1514).

Like the other alkali metals, potassium does not obey the Debye formula which requires a constant value for the Debye characteristic temperature, θ. Instead, θ shows a marked temperature-dependence. General theoretical treatments of the specific heat of the alkali metals have been discussed under 'Lithium' and 'Sodium' (see pages 38 and 393).

Values of the characteristic temperature for potassium have been given by a number of authors in treatments of specific heat and other data.[72,73,138-139b,143-146a] In a recent detailed study of characteristic temperatures,[144,145] four different methods have been used for calculating θ_D, the Debye characteristic temperature, from thermodynamic data and θ_R from electrical resistance data: curves of these as a function of temperature have been given up to 300°K. in the case of θ_D and 150°K. in the case of θ_R.

Heat Content or Enthalpy.

Recent calorimetric measurements[100] using pure potassium have led to the following equations for the heat content or enthalpy of the metal in the solid and liquid states. The enthalpy is in absolute joules per gram, the temperature in degrees centigrade, and the probable error for the two equations has been estimated as ±1–2% and ±0·3% respectively.

$$H_t(\text{solid}) - H_0(\text{solid}) = 0{\cdot}71040t + 1{\cdot}0385 \times 10^{-3}t^2 \quad (0^\circ \text{ to } 63{\cdot}2^\circ\text{C.})$$

$$H_t(\text{liq.}) - H_0(\text{solid}) = 56{\cdot}179 + 0{\cdot}840741t - 1{\cdot}58440 \times 10^{-4}t^2 + 1{\cdot}04993 \times 10^{-7}t^3 \quad (63{\cdot}2^\circ \text{ to } 800^\circ\text{C.})$$

Enthalpy values for rounded temperatures obtained by using these equations are included in Table VII, whilst Table VIII shows values for the heat content function of potassium selected in a recent summary[137] of thermodynamic data for the alkali metals. On the basis of data available up to 1948, Kelley[142] formulated the following equations to represent the enthalpy of solid and liquid potassium within ±1%, the enthalpy being in g.-cal./g.-atom and T in °K.

TABLE IX. - THERMODYNAMIC FUNCTIONS FOR MONATOMIC AND DIATOMIC POTASSIUM VAPOUR IN THEIR STANDARD STATE OF ONE ATMOSPHERE PRESSURE

T, °K.	$-\left(\frac{F^\circ-E_0^\circ}{T}\right)_1$ g.-cal./mole/°K.	$-\left(\frac{F^\circ-E_0^\circ}{T}\right)_2$ g.-cal./mole/°K.	$\left(\frac{H^\circ-E_0^\circ}{T}\right)_1$ g.-cal./mole/°K.	$\left(\frac{H^\circ-E_0^\circ}{T}\right)_2$ g.-cal./mole/°K.
100	27·900	41·992	4·9680	7·9295
298·16	33·327	51·059	4·9680	8·6048
335·5	33·913	52·077	4·9680	8·6565
500	35·895	55·563	4·9680	8·8123
760	37·975	59·283	4·9680	8·9604
1000	39·339	61·757	4·9680	9·0592
1200	40·244	63·415	4·9680	9·1296
1400	41·010	64·827	4·9680	9·1942
1600	41·674	66·059	4·9680	9·2548
1800	42·259	67·152	4·9680	9·3131
2000	42·783	68·136	4·9680	9·3695
2200	43·257	69·032	4·9680	9·4247
2400	43·691	69·854	4·9680	9·4788
2600	44·090	70·615	4·9680	9·5323
2800	44·461	71·324	4·9680	9·5851
3000	44·809	71·987	4·9680	9·6375

T. °K.	S_1° g.-cal./mole/°K.	S_2° g.-cal./mole/°K.	C_{p1}° g.-cal./mole/°K.	C_{p2}° g.-cal./mole/°K.
100	32·868	49·922	4·9680	8·7207
298·16	38·295	59·664	4·9680	9·0565
335·5	38·881	60·734	4·9680	9·0817
500	40·863	64·375	4·9680	9·1769
760	42·943	68·243	4·9680	9·3117
1000	44·307	70·816	4·9680	9·4320
1200	45·212	72·545	4·9680	9·5314
1400	45·978	74·021	4·9680	9·6305
1600	46·642	75·314	4·9680	9·7294
1800	47·227	76·465	4·9680	9·8282
2000	47·751	77·506	4·9680	9·9268
2200	48·225	78·457	4·9680	10·0255
2400	48·659	79·333	4·9680	10·1241
2600	49·058	80·147	4·9680	10·2227
2800	49·429	80·909	4·9680	10·3213
3000	49·777	81·625	4·9680	10·4020

Subscript (1) refers to monatomic potassium vapour and subscript (2) to diatomic potassium vapour

$$H_T(\text{solid}) - H_{298\cdot16}(\text{solid}) = 6\cdot04T + 1\cdot56 \times 10^{-3}T^2 - 1940 \quad (298^\circ \text{ to } 336\cdot7^\circ\text{K.})$$
$$H_T(\text{liq.}) - H_{298\cdot16}(\text{solid}) = 7\cdot80T - 1781 \quad (336\cdot7^\circ \text{ to } 600^\circ\text{K.})$$

From vibrational frequency data, Kelley[142] represented the enthalpy (in g.-cal./g.-mole) of diatomic potassium vapour between 298° and 2000°K. within ±0·5% by the equation:-

$$H_T - H_{298\cdot16} = 8\cdot94T + 0\cdot03 \times 10^5 T^{-1} - 2676$$

Using spectroscopic data and assuming the vapours to behave as ideal gases the values of Table IX have been calculated for the enthalpy function and other thermodynamic properties of both monatomic and diatomic potassium vapour.[126] Other calculations[137] have given very similar values.

Entropy.

From the low-temperature heat capacity measurements of Simon and Zeidler[138] the entropy of solid potassium at 298·16°K. has been calculated[146] to be 15·2 ± 0·2 g.-cal./g.-atom/°K. The U.S. Bureau of Standards also take 15·2 as the selected value at 298·16°K.[136] Other more recent heat capacity measurements[139a] lead to entropy values at 273·16°K. and 298·16°K. of 14·77 ± 0·03 g.-cal./g.-atom and 15·38 ± 0·03 g.-cal./g.-atom respectively. From heat capacity measurements[100] between 0° and 800° C. the following equations have been derived for solid and liquid potassium: (S in joules/g./degree; T in °K.).

$$S_T(\text{solid}) - S_{273{\cdot}16^\circ\text{K.}}(\text{solid}) = 0{\cdot}32938 \log T + 2{\cdot}0770 \times 10^{-3}T - 1{\cdot}36986 \quad (273^\circ \text{ to } 336{\cdot}4^\circ\text{K.})$$

$$S_T(\text{liq.}) - S_{273{\cdot}16^\circ\text{K.}}(\text{solid}) = 2{\cdot}18919 \log T - 4{\cdot}8862 \times 10^{-4}T + 1{\cdot}5718 \times 10^{-7}T^2 - 5{\cdot}04665 \quad (336{\cdot}4^\circ \text{ to } 1073^\circ\text{K.})$$

Values at rounded temperatures calculated from these equations are included in Table VII. Table VIII lists entropy values[137] between 0° and 1000°K.

For monatomic potassium vapour, the Sackur equation – with Rln 2 added to account for the multiplicity in the lowest energy state – gives 38·30 ± 0·01 g.-cal./g.-atom/°K. for the entropy at 298·16°K.[146] For diatomic potassium, $S^\circ_{298{\cdot}16} = 59{\cdot}55 \pm 0{\cdot}10$ g.-cal./g.-mole/°K. has been obtained from the moment of inertia and the vibration frequency; the vibrational contribution is 3·617 and the translational and rotational contribution 55·929. Other values for the entropy of monatomic and diatomic potassium vapour calculated for temperatures of 100° to 3000°K. using spectroscopic data are shown in Table IX.[126] Values calculated up to somewhat lower temperatures by other authors[137] agree closely with them.

Free Energy.

Free energy data for potassium in the solid, liquid and gaseous states are included in or may be derived from the data of Tables VII,[100] VIII[137] and IX.[126]

Thermal Conductivity

Low temperature studies have shown a substantially constant thermal conductivity of around 1 watt cm.$^{-1}$degree^{-1} between 25° and 90°K.[146a] Below 25°K. it rose rapidly to a maximum of 5 to 7 watt cm.$^{-1}$degree^{-1} at about 5°K. At temperatures below 16°K. the thermal conductivity was represented by the equation:-

$$1/k = A/T + 1{\cdot}7 \times 10^{-3}T^2$$

where A for three different potassium specimens had values between 0·52 and 0·85. No new determinations of the thermal conductivity of solid potassium at ordinary temperatures have been reported.

Measurements of the thermal conductivity of liquid potassium have been made between ~175° and 610°C., and over this range the conductivity varied linearly with temperature.[147] The experimental values were also closely fitted by the equation $k/C_pd^{5/3}$ = constant, where k is the thermal conductivity, C_p the specific heat and d the density. This equation has been used to extrapolate values up to 800°C. A selection of values for the thermal conductivity of liquid potassium is given in Table X.[147] Thermal conductivities calculated from measurements[55a] of thermal diffusivity (= k/C_pd) between the melting point and 630°C. approximate to those of Table X at the higher temperatures but are appreciably higher (~15%) at the lower temperatures.

From generalized relationships between electrical and thermal conductivity,

TABLE X.- THERMAL CONDUCTIVITY OF LIQUID POTASSIUM

Temp., °C.	200	300	400	500	600	700	800
k(watt/cm.°C.)	0·454	0·424	0·397	0·374	0·356	0·340	0·326

an estimate of 0·15 to 0·20 g.-cal.cm.$^{-1}$sec.$^{-1}$deg.$^{-1}$(0·63 to 0·84 watt/cm./deg.) has been made for the thermal conductivity of liquid potassium at its melting point.[148]

Electrical Resistance

McLennan and Niven[149] gave the specific resistance of potassium at 273°K. as $6{\cdot}1 \times 10^{-6}$. At 191°, 80° and 20·6°K. the values were $4{\cdot}0 \times 10^{-6}$, $1{\cdot}6 \times 10^{-6}$ and $0{\cdot}35 \times 10^{-6}$ respectively. McDonald and co-workers[146a] obtained values of $6{\cdot}4 \times 10^{-6}$, $7{\cdot}0 \times 10^{-6}$ and $10{\cdot}8 \times 10^{-6}$ ohm cm. for the specific resistance of three different samples of potassium at 295°K. Bidwell[150] measured the resistance (relative to that at 0°C.) of potassium contained in capillary tubes over the range -150°C. to +100°C. His results are shown in Fig. 2; there is a slight break in the curve at about -110° to -120°C., and a marked increase in the $R/R_{0°C.}$ ratio at the melting point.

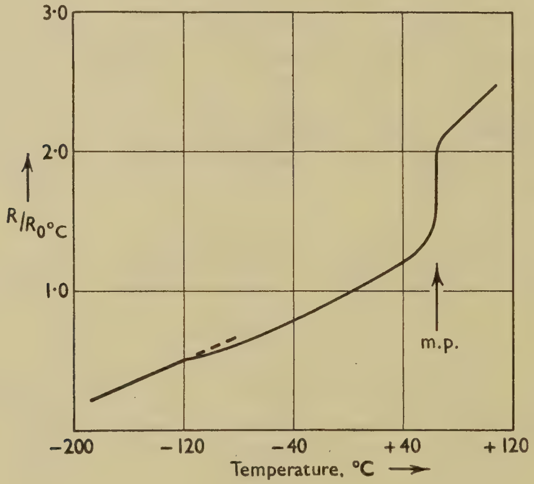

FIG. 2. RELATIVE ELECTRICAL RESISTANCE OF POTASSIUM

Several workers have measured the resistance of potassium at low temperatures relative to that at 273°K.[143,146a,151-154] The value of the $R/R_{273°K.}$ ratio is greatly affected by the presence of small amounts of impurity, and the magnitude of the ratio at temperatures approaching absolute zero gives an indication of the purity of the samples used. The purer the sample, the lower is the ratio. Approximate residual resistance ratios for the samples used by the various workers were 0·007,[151] 0·09,[152] 0·024 and 0·003,[153] 0·001 to 0·00056,[154] 0·1 to 0·007,[143] and 0·002 to 0·003.[146a] Table XI shows the $R/R_{273°K.}$ ratios for one of the purer of these samples after subtracting the residual resistance ratio (~0·003).[153]

From 3° to 7°K. the resistance, corrected for the residual resistance, is a fifth power of the absolute temperature.[153] The power decreases at higher

TABLE XI.- RELATIVE ELECTRICAL RESISTANCE OF POTASSIUM AT LOW TEMPERATURES

Temp., °K.	3·02	4·13	5·25	7·88	9·35
R/R_{273}°K.	0·000008	0·000047	0·000166	0·000921	0·001737
Temp., °K.	11·41	14·23	16·0	18·84	20·33
R/R_{273}°K.	0·003332	0·006693	0·009542	0·015371	0·019110

temperatures, and between 14° and 20°K. a T^3 law applies. MacDonald and Mendelssohn[143] measured the resistance ratio for seven samples of potassium of various purities; for samples with residual resistance ratios ranging from 0·1 to 0·0145 there were slight anomalous humps in the relative resistance curve at temperatures of ~12° and 10°K., but these disappeared in the purest sample (residual resistance ratio ~0·007). It was also found that for this purest sample resistance varied directly as T^3 from 20°K. down to 8°K. and as T^5 below 6·5°K.

Kamerlingh Onnes and co-workers[155,156] showed that potassium was not superconducting down to a temperature of 1·5°K., and later work has shown that this is also true down to 0·08°K.[157,158]

The electrical resistivity of thin films of potassium deposited on clean glass surfaces in high vacuum has been studied as a function of film thickness and of temperature.[159-161] In thin films the resistivity is much greater than that of the bulk metal. Deposition of the film took place by directing a beam of potassium atoms onto a surface cooled to between 64° and 90°K., and a continuous series of resistance measurements were made during and after deposition. With increasing thickness of the layer, the resistance and resistivity decreased steadily, but on stopping deposition the resistance did not remain constant but (for a film thickness of ~20A.) increased in the course of half an hour by a factor of about 30. The decay of conductivity on stopping deposition was attributed to the widening of cracks and imperfections in the film under the action of surface tension forces. Potassium films were much less stable in this respect than were those of rubidium and caesium. Fig. 3 compares the formation and decay of conductivity for ~20A. films of potassium, rubidium and caesium deposited at 90°K. with approximately the same beam intensity in each case.[159]

For potassium, conductivity began at a film thickness of about 3·2A., and with the film 20A. thick the resistivity was approximately 34,000 times that of the metal in bulk. The decay of conductivity after cessation of deposition decreases with increasing film thickness and with decreasing temperature. At 64°K. a film of potassium 40A. thick borders on the verge of instability. Potassium films 2000A. thick have a resistivity which is still two or three times that of the bulk metal, but the temperature coefficient is the same as for the bulk metal.[161] For the films with thicknesses below 100A. the greatly increased resistivity is attributed to limitation of the mean free path of the conduction electrons by the boundaries of the film, but for the films with thicknesses of the order of 10^3A. the increase in resistivity over that of the metal in bulk is attributed to lattice strain.[161]

Measurements have also been made of the conductivity of alkali metal films (probably monatomic) deposited spontaneously on the glass walls of vessels containing the metal in vacuo.[162] The conductivity of the films increases in the order K, Rb, Cs.

The effect of magnetic fields with strengths up to 35 kilogauss on the electrical resistance of potassium was studied by Justi[154] at temperatures between 4·2°C. and 20·4°K. The percentage change in resistance on application of the fields is dependent to a large extent on the purity of the sample.

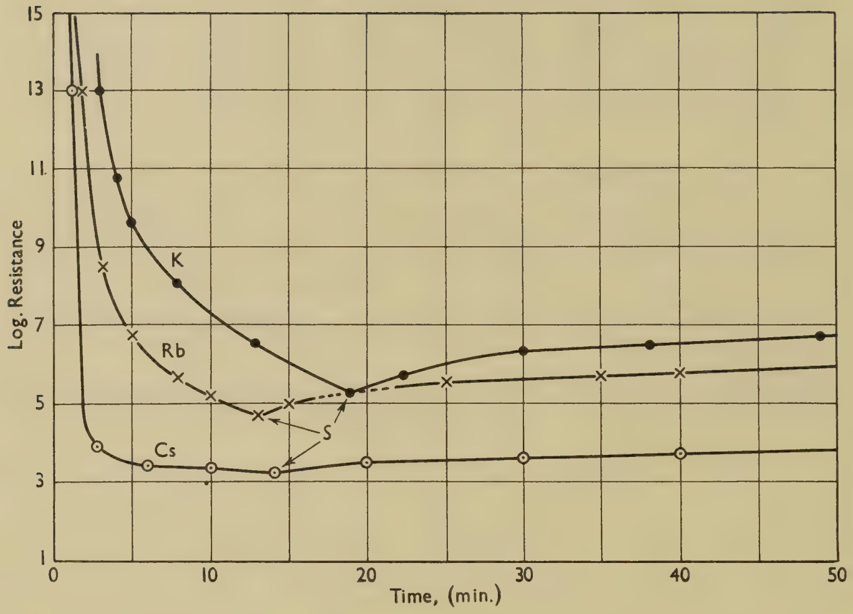

FIG. 3. FORMATION AND DECAY OF CONDUCTIVITY FOR FILMS OF K, Rb, Cs DEPOSITED AT 90°K. ●K: 20A. WITH BEAM INTENSITY $2{\cdot}45 \times 10^{12}$ atoms/cm.^{2}/sec.; × Rb: 21•8A. WITH BEAM INTENSITY $3{\cdot}15 \times 10^{12}$ atoms/cm.^{2}/sec.; ⊙ Cs: 21•0A. WITH BEAM INTENSITY $2{\cdot}30 \times 10^{12}$ atoms/cm.^{2}/sec. S: SHUTTER CLOSED (CESSATION OF DEPOSITION)

For one particular sample at 14°K. a longitudinal field of 16•5 kilogauss gave a 1•95% increase in resistance, while a transverse field of the same strength gave a 2•49% increase.

Earlier measurements (Mellor,II,460) of the effect of pressure on the electrical resistance of potassium have been extended to higher pressures.[163-166] Table XII shows the results of measurements at 30°C. for pressures up to 30,000 kg./cm.^{2}.[165]

TABLE XII. - EFFECT OF PRESSURE ON THE ELECTRICAL RESISTANCE OF POTASSIUM

Pressure, kg./cm.^{2}	0	2,500	5,000	10,000	15,000	20,000	21,000
$R/R_{\text{zero pressure}}$	1•0	0•664	0•491	0•303	0•219	0•1821	0•1788
Pressure, kg./cm.^{2}	22,000	23,000	24,000	25,000	26,000	28,000	30,000
$R/R_{\text{zero pressure}}$	0•1760	0•1740	0•1726	0•1719	0•1721	0•1740	0•1778

In 1930, Bridgman[164] found no minimum in the resistance–pressure curve up to 19,500 kg./cm.^{2}, but extrapolation indicated a minimum relative resistance of about 0•175 at 23,500 kg./cm.^{2} His later work[165] at higher pressures confirmed the existence of a minimum which at 30°C. was found to have a value of ~0•172 and to occur at 25,400 kg./cm.^{2} At 25°C. the minimum occurs at about 25,000 kg./cm.^{2} Further measurements[166] up to 100,000 kg./cm.^{2} have shown a progressive increase of $R/R_{\text{zero pressure}}$ with pressure in the region above this minimum:-

Pressure, kg./cm.^{2}	30,000	40,000	50,000	60,000
$R/R_{\text{zero pressure}}$	0·178	0·203	0·252	0·309

Pressure, kg./cm.^{2}	70,000	80,000	90,000	100,000
$R/R_{\text{zero pressure}}$	0·370	0·439	0·514	0·596

Potassium vapour at 1200° C. has an electrical conductivity of 10^{-19} ohm^{-1} cm.$^{-1}$ at a pressure of one atmosphere, and 10^{-5} ohm^{-1}cm.$^{-1}$ at ten atmospheres.[167] There is no evidence of metallic conduction under these conditions.

Several theoretical treatments of the electrical conductivity of potassium have appeared.[168-170a]

Thermoelectric Properties

The thermoelectric power of potassium relative to platinum was measured by Bidwell[150] over the range −180° to +110°C.: the results are shown in Fig. 4. A marked break occurs in the thermoelectric power-temperature curve at about −120°C. There is also a considerable increase in thermoelectric power as the melting point is approached; above the melting point the thermoelectric power decreases with increase of temperature.

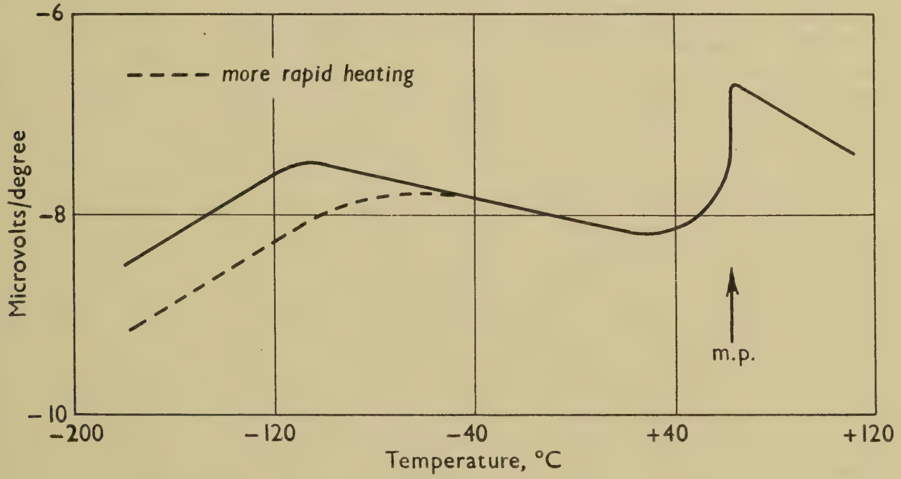

FIG. 4 THERMOELECTRIC POWER OF POTASSIUM

MacDonald and Pearson[171,172] measured the thermoelectric force of potassium against lead at temperatures below ~80°K. Using the absolute thermoelectric force of lead as measured by Borelius *et al.*,[173] the following values (interpolated from their graphically presented results) were obtained for the absolute thermoelectric force of potassium:-

T, °K.	10	20	30	40	50	60	70
Microvolts	0	−6	−20	−43	−72	−106	−145

Below ~30°K. the thermoelectric power is proportional to the square of the temperature. Above this point the temperature dependence falls to well below a linear power law.[171] The thermoelectric effect of the alkali metals has been discussed from the viewpoint of the electron theory of metals.[171,172,174]

Magnetic Properties

Potassium is paramagnetic, its susceptibility varying only slightly with temperature. The earlier value of 0·40 × 10^{-6} (Mellor, II, 460) for the mass susceptibility now appears to be slightly too low. More recent values for the mass susceptibility at room temperature have included 0·49 × 10^{-6},[175] 0·51 × 10^{-6},[176] 0·54 × 10^{-6},[177] 0·55 × 10^{-6},[6] and 0·532 ± 0·002 × 10^{-6}.[178] There is a slight fall in susceptibility on passing from the solid to the liquid state: the value for the liquid has been observed to increase from 0·50 × 10^{-6} at the melting point to 0·53 × 10^{-6} at 500°C.[176] Neumann[179] obtained a volume susceptibility of 0·40 × 10^{-6} at 21·5°C. which is equivalent to a mass susceptibility of 0·47 × 10^{-6}. Böhm and Klemm[6] have given the following values for the atomic susceptibility (mass susceptibility × atomic weight) of potassium between −183° and +100°C.:-

t, °C.	−183	−78	+20	+100
$\chi_{At} \times 10^6$	20·0	20·3	21·5	20·4

A value[180] of −1·9 × 10^{-6} for the atomic susceptibility of potassium is at variance with the results of all subsequent workers.

Theoretical computations[181,182] of the magnetic susceptibility of potassium have been made.

Electron spin resonance absorption has been sought in potassium.[92a,182a] Gutowsky and Frank[182a] working at a frequency of ~25 Mc./sec. detected no resonance at room temperature or at 77°K. Feher and Kip[92a] who investigated the resonance absorption of metals at 300 and 9000 Mc./sec. for temperatures between 4° and 296°K., obtained a signal with potassium only at 4°K. and 300 Mc./sec. and even this was very weak. That part of the volume susceptibility arising from conduction electron spins has been calculated by Pines[182b] to be 0·61 × 10^{-6} c.g.s. units.

Many attempts have been made to evaluate the contribution of the potassium ion towards the diamagnetism of its salts both from purely theoretical considerations and by making use of experimental data on the susceptibility of salts. A wide variety of values has resulted from the efforts of the various authors. Values for the susceptibility of the potassium ion in solution obtained from measurements on its salts include −17·5,[183] −17·4,[184] −16·9,[185] −16·5,[186,187] −16·3,[188] −14·0,[189,190] and −13·5,[191] (all to be multiplied by 10^{-6}), while values for the K^+ ion in crystals include −14·6 × 10^{-6},[192,193] and −13·6 × 10^{-6}.[194] Theoretical treatments have given the following values for free potassium ions: −20·0,[195] −19·06,[196] −18,[197] −17·61,[198] −16·7,[199] −14·5,[200] −14·4,[191,201] −14·2,[193] −13·06,[202] and −8·4,[203] (all to be multiplied by 10^{-6}). Other values for the free ion include −17·5,[183] −17·4,[184] −16·5,[186,187] and −16·3,[188] (all to be multiplied by 10^{-6}). In reviewing the field, Klemm[204,205] gave −11·4 × 10^{-6} as the most probable value for the susceptibility of the potassium ion in solution; for the ion in crystals he gave −12·9 × 10^{-6} when the co-ordination number is 6 and −12·8 × 10^{-6} when it is 8; for the free ion he gave −14·0 × 10^{-6}. Another contemporary survey[206] recommends −14·9 × 10^{-6} without distinguishing between the ion in solution and in crystals.[207] Methods of obtaining ionic susceptibilities and/or the values resulting from them have been reviewed by several authors.[204,206,208-210]

From the deflection pattern obtained when a beam of potassium atoms is passed through a non-homogeneous magnetic field[211-215] or is passed obliquely through a homogeneous field[216] potassium is found to have a magnetic moment of one Bohr magneton.

Several determinations are in agreement in giving 0·391 nuclear magnetons for the moment of the ^{39}K nucleus.[217-220] A number of other authors[221-226] have measured or have discussed the nuclear magnetic moment of ^{39}K; most of the values fall between 0·38 and 0·40 nuclear magnetons. Values of[219] 0·215 and[237] 0·22 nuclear magnetons have been given for the moment of the ^{41}K

nucleus.

The nuclear spin of both ^{39}K and ^{41}K is 3/2.[222,223,236,237]

Electrode Potentials

Because of the reaction between potassium and water, an indirect method is necessary for the determination of the standard electrode potential of potassium (see page 404). The European convention regarding the sign of the electrode potential is followed for all the values quoted below. A recalculation[238] of the results of Lewis and Keyes[239] who measured the e.m.f. of the cells:-

K (solid) | KI in ethylamine | K (0·2216% amalgam)
and K (0·2216% amalgam) | KOH aq.; KCl aq. | Calomel electrode

has given −2·9224V. as the standard potential of potassium at 25°C. on the hydrogen scale. A combination of Lewis and Keyes' value (1·0487V.) for the e.m.f. of the above non-aqueous cell with other later measurements of the potential of potassium amalgam electrodes[240] has led to −2·9243V. for the standard potential of potassium.[240] Thermodynamic calculations of the standard potential have been made by Drossbach,[241-243] who finally arrived at E°_{K} = −2·97 or −2·96V. From measurements of the decomposition voltages of fused potassium halides a value of −2·614V. has been given for the potential of potassium extrapolated to 18°C.[244] Using spectroscopic and thermodynamic data, Gapon[245] calculated a value of +0·96V. for the absolute electrode potential of potassium. An earlier determination of the absolute potential was reported by Scarpa.[246]

The best representative values for the standard electrode potentials of the alkali metals in aqueous solution at 25°C. are compared on page 405.

As with sodium, the standard electrode potential of potassium in non-aqueous solvents appears in general to be less negative than in water. In nitrobenzene the standard potential has been given as −2·804V.;[247] in ethyl bromide it has been given as −2·516V.[248] Other measurements of the potassium electrode potential have been made in formamide,[248a] liquid ammonia,[249-251] hydrazine[252] and formic acid.[253] Electrode potentials of the alkali metals in the last three solvents and in water are compared on page 47.

Values for the electrode potential of potassium relative to that of other metals in various fused halide electrolytes have been obtained by direct measurement or by calculation from thermodynamic data, and electrochemical series have been developed.[253a,253b] The order of the metals in the series varies with the anion and with temperature, and in the case of mixed salts it may also be affected by complex formation.

The interest in potential measurements on potassium amalgam electrodes as a stage in the determination of the standard electrode potential of potassium has been referred to above. Several authors have made extensive studies of potassium amalgam electrodes.[240,254-257] Armbuster and Crenshaw[240] measured the e.m.f. of potassium amalgam concentration cells at 15°, 25° and 35°C. over a wide range of potassium concentrations using aqueous electrolytes and dropping electrodes. From their results they derived the following equations for the e.m.f. (in volts) of amalgams of potassium mole fraction N measured against an amalgam of mole fraction 0·019844:-

$$\frac{-E_{15^\circ\,\mathrm{C.}}}{0{\cdot}057153} - \log N = 1{\cdot}0900 + 28{\cdot}9885N - 3{\cdot}90N^2 + 5367N^3$$

$$\frac{-E_{25^\circ\,\mathrm{C.}}}{0{\cdot}059135} - \log N = 1{\cdot}1056 + 27{\cdot}705N + 123{\cdot}02N^2$$

$$\frac{-E_{35^\circ \mathrm{C.}}}{0{\cdot}061119} - \log N = 1{\cdot}1218 + 26{\cdot}478N + 130{\cdot}37N^2 + 564{\cdot}0N^3$$

Measurements[240] of a potassium amalgam electrode ($N = 0{\cdot}002559$) against calomel and silver chloride electrodes gave the following results:-

K amalgam $N = 0{\cdot}002559$	KCl aq. 0·10245M.	HgCl | Hg	$E_{25^\circ \mathrm{C.}} = 2{\cdot}2217$V.
K amalgam $N = 0{\cdot}002559$	KCl aq. 1·0168M.	AgCl | Ag	$E_{25^\circ \mathrm{C.}} = 2{\cdot}0704$V.

Amalgams with a potassium concentration less than 0·01 wt.-% were found to give unreliable e.m.f. values, while those between 0·02 and 0·4 wt.-% gave values reproducible to 0·02mV. Bent and Gilfillan[256] measured the e.m.f. of potassium amalgam concentration cells as a function of concentration and temperature using several electrolytes viz., aqueous potassium hydroxide solutions, ether solutions of potassium addition compounds of organic free radicals, and solutions of potassium iodide in ethylamine. Combining their results with Lewis and Keyes'[239] measurement of the e.m.f. of an amalgam electrode against solid potassium, the activity, *a*, of potassium in its amalgams – referred to the solid metal as standard state – was represented by the equation:-

$$\log a/N = -5695{\cdot}6/T - 27{\cdot}69/T^{0{\cdot}77700} + 3{\cdot}3249 + 2446/T^{0{\cdot}77700}\{N + 3{\cdot}3430N^4\} \pm 0{\cdot}0017,$$

N being the mole fraction of potassium in the amalgam, and T the temperature in °K. Activities of potassium in its amalgams have also been determined[258] at 325°C. using the cell K | Thüringer glass | K/Hg.

Potentials of amalgam cathodes during the deposition of potassium from concentrated solutions of its chloride and hydroxide have been reported by Esin *et al.*[259,260]

Heyrovsky[261,262] studied the behaviour of potassium ions at the dropping mercury cathode in his first polarographic experiments; he gave the deposition potential at mercury from aqueous solution as −1·883V. relative to a normal calomel electrode. The formation of compounds between potassium and mercury, together with the high hydrogen overvoltage at mercury, makes possible the discharge of potassium ions at a mercury cathode in acid and neutral solutions despite the very negative standard potential of potassium. The negative potential does, however, limit the choice of supporting electrolyte; tetra-alkylammonium halides or hydroxide are commonly employed.[263] With tetramethylammonium chloride or hydroxide as the supporting electrolyte, the half-wave potential of potassium ions in aqueous solutions is −2·17V. relative to a normal calomel electrode.[264,265] More precise studies in 0·1M. tetramethylammonium hydroxide solution at 25°C. have given the half-wave potential as $-2{\cdot}166_5$V. against a normal calomel electrode.[265a,265b] Alcohol-water mixtures are frequently used in obtaining polarograms of the alkali metals since these give better developed waves than do purely aqueous media.[266-268] In 50% ethyl alcohol at 25°C., with 0·1M. tetraethylammonium hydroxide as supporting electrolyte, the half-wave potential of potassium ions relative to a saturated calomel electrode is −2·10V.; in 80% ethyl alcohol it is −2·05V.[267,268] The half-wave potentials of potassium, sodium, rubidium and caesium (Na, −2·07V.; Rb, −1·99V.; Cs, −2·05V.; all in 50% ethyl alcohol + 0·1M. tetraethylammonium hydroxide) are so close to one another that these four alkali metals cannot be differentiated polarographically.[263] Colloidal materials such as gelatin and agar-agar tend to cause the deposition potentials of the alkali metals at a dropping mercury cathode to become less negative.[269] Polarographic waves in ethylene glycol, trimethylene glycol, glycerol and in dioxan–water mixtures have also been studied.[266]

In liquid ammonia at –36°C., saturated with tetrabutylammonium iodide as supporting electrolyte, the half-wave potential of potassium ions is –1·24V. relative to a 0·1N.$Pb/Pb(NO_3)_2$ reference electrode.[270]

Ionization Potentials, Electron Affinity and Electronegativity

Ionization potentials for potassium have been arrived at either by calculation from spectral series limits or by extrapolation along the isoelectronic sequences. The values in the second column of Table XIII are based on the compilation of Moore[271] as revised and extended by Finkelnburg;[272] those in the third column are from another recent compilation.[273]

TABLE XIII.- IONIZATION POTENTIALS OF POTASSIUM IN ELECTRON VOLTS

I	4·339	4·34
II	31·81	31·7
III	46·1	45·5
IV	60·9	60·6
V	82·5	(83)
VI	99·88	(101)
VII	118·24	(120)
VIII	154·6	(155)
IX	175·8	176·0
X	504·1	501·4
XI	566·2	–
XII	630·2	–
XIII	717·7	–
XIV	789·9	–

Ionization of potassium vapour can result in various ways, for example, by the action of light (see page 1529) by electron impact,[274-278] and thermally.[279-282] Ionization on hot surfaces of tungsten and other metals has been investigated by a number of workers.[113,283-299]

Hartree and Hartree,[300] from self-consistent field calculations of wave functions for the negative K^- ion, deduced that this ion could exist and was probably stable. A recent estimate[301] of +0·7 e.V. for the electron affinity is in conformity with a stable K^- ion. Such ions have been reported from mass spectrometer studies.[274,302]

Potassium has a value of 0·8 on Pauling's electronegativity scale, values for the other alkali metals being Li, 1·0; Na, 0·9; Rb, 0·8; and Cs, 0·7.[44]

Optical Properties

Whilst thin films of potassium are opaque to visible light they are highly transparent in the ultra-violet region of the spectrum. Transparency commences at a wave-length around 3150A.,[303,304] and there is no renewal of reflecting power as far as 500A.[305] A film of potassium, several wave-lengths thick, through which the sun's disk is barely visible (*i.e.* the intensity is reduced by a factor of about half a million) is reported to transmit 25% of all light with wave-length shorter than 3000A.[303] In the transparent region the metal surface yields plane polarized light by reflexion of ordinary light at an angle in accordance with Brewster's law.[303] From measurements of the reflecting power and the Brewsterian angle for plane polarization, Wood[303] calculated values for the refractive index of potassium ranging from 0·90 at 2147A. to 0·50 at 3100A.

Ives and Briggs[306] studied the reflexion of monochromatic plane polarized light from potassium surfaces, and from measurements of the phase shift and the azimuth of restored linear polarization they calculated values for the refractive index (n), the extinction coefficient (K_0), and the reflecting power for normal incidence (R). Table XIV shows their results.

TABLE XIV. - OPTICAL CONSTANTS OF POTASSIUM

Wave-length (A.)	n	K_0	$R(\%)$
5780	0·094	1·57	89·8
5461	0·091	1·42	88·7
4358	0·121	0·978	78·1
4047	0·105	0·710	73·2
3650	0·150	0·443	60·7
3126	0·410	0·080	18·2
2536	0·744	0·049	2·61

Transmission curves for potassium films of several thicknesses calculated from the above results are shown in Fig. 5.[306]

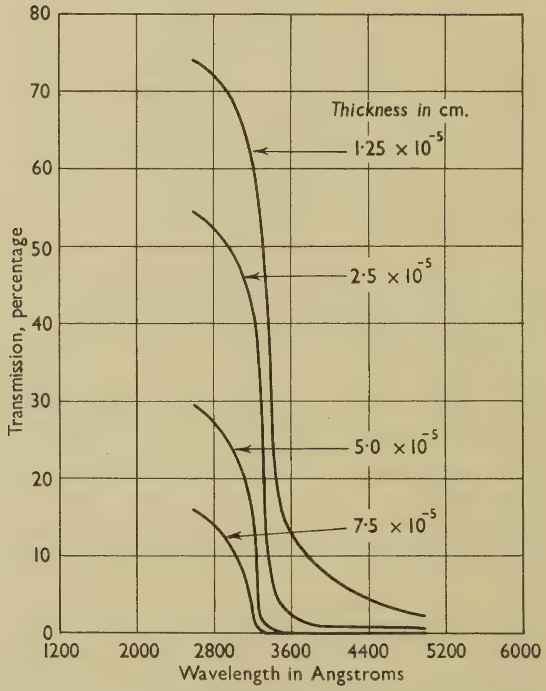

FIG. 5. OPTICAL TRANSMISSION FOR POTASSIUM FILMS OF SEVERAL THICKNESSES

Other studies have given ~0·06 for the refractive index of potassium using light of $\lambda = 5461$A.[307] and ~0·09 for light of $\lambda = 5890$A.[308] The optical properties of liquid potassium have been shown to be almost identical with those of the solid.[307,308]

Optical properties of very thin (0·5 to 40mμ thick) films of potassium have been studied by Hacman.[309-311] The refractive index and extinction coefficient vary with film thickness, and for the thinner films both show pronounced maxima at wave-lengths in the region of 3600 to 3800A.

Theoretical treatments of the optical properties of potassium and the other alkali metals have been made by several authors:[312-318a] in particular, attention has been paid to the explanation of the transparency in the ultra-violet region.

Studies have been made of anomalous dispersion in potassium vapour in the region of the first (red) and second (violet) doublets of the principal series,[319-322] and of magnetic double refraction (Voigt effect) in potassium vapour at various pressures.[323]

Photoelectric Properties

The photoelectric threshold of potassium is very sensitive to the conditions of measurement. It varies with the state of the surface and with film thickness, and is greatly affected by the presence of even slight traces of gas. The extreme sensitivity to small amounts of impurity makes it difficult to isolate the true photoelectric behaviour of the pure metal, and many effects that have been observed with supposedly pure metal are probably dependent on the presence of adsorbed gases. Several books concerned with photoelectricity have paid considerable attention to potassium and other alkali metals.[324-327]

For thick layers of potassium the threshold wave-length appears to be in the region of 5500A. which corresponds to a photoelectric work function of 2·24 e.V.[328] Other values of[329] ~2·20 and 2·26 e.V.[330] have been given for the work function of thick, gas-free, potassium layers. Partially outgassed samples have given various values between 1·7 and 2·2 e.V.[331] Theoretical values for the work function have included[332] 2·20 and 2·09 e.V.[333]

When polarized light with its electric vector perpendicular to the plane of incidence is employed, the photoelectric emission increases steadily with decreasing wave-length at least to 1850A.; but with the electric vector in the plane of incidence, maxima at visible or near ultra-violet wave-lengths have been observed.[334-337] This is known as a selective effect. A maximum emission at 4360A. has been reported[336,337] for light with the electric vector in the plane of incidence, but it appears that this is not obtained with potassium of the highest purity.[337] Fleischer,[337] using a rigorously outgassed sample, found (for light with the E vector in the plane of incidence) maxima at 3130A. in both the light absorption and the photoelectric current curves, but when the photoelectric current was expressed in terms of light absorbed the maximum disappeared. On the other hand, the maximum in the photoelectric current which could be produced at 4360A. by adsorption of hydrogen on the surface, remained when expressed in terms of light absorption.[337] Ives and Briggs[338] observed a close similarity between the light absorption and spectral response curves for potassium films on platinum–iridium mirrors, both exhibiting a maximum at about 3400A. More recent spectral sensitivity measurements on very pure compact potassium have given a maximum around 4000A. with the sensitivity expressed in terms of incident light; in terms of light absorbed the sensitivity rose sharply from the long wave limit at 5500A. up to 4000A. and thereafter remained essentially constant.[338a]

For potassium distilled a number of times in high vacuum a photoelectric yield of 5–10 × 10^{-5} coulombs per calorie of incident light has been obtained in the region of maximum sensitivity at 4400A.[339] The spectral response curve for another specimen of freshly distilled potassium is included in Fig. 6[340] (see page 1527). A pure sample of compact potassium gave 2–5 × 10^{-4} coulombs per calorie in the region of the maximum at ~4000A.[338a]

The initial effect of the deposition of potassium onto a metal substrate is to shift the photoelectric response of the substrate to longer wave-lengths.

With increasing thickness the threshold wave-length passes through a maximum and then returns to that for bulk potassium. The photoelectric emission continues to increase with increasing thickness up to greater thicknesses before dropping to the emission for the bulk metal. On a silver substrate, Brady,[328] working at −180°C., found a maximum threshold of 5800A. at a thickness of 3 atomic layers, a final threshold at 5500A., and the maximum total photoelectric emission at 12·4 atomic layers. For films with thicknesses greater than 19 atomic layers the photoelectric properties were those of bulk potassium. These thickness estimates have since been considered to be too high because of the neglected roughness of the substrate.[341] Another study[342] has also given 5800A. for the maximum threshold of potassium on silver, the maximum selective effect being observed at 3430A. for an estimated film thickness greater than one monatomic layer. Ives and Olpin[343] reported the maximum threshold for potassium on silver to be 7700A., close to the first line of the principal series (7899A.), a relationship that they also found for the other alkali metals. It has, however, been considered probable[344] that their substrate contained some oxygen which is known to cause large threshold shifts. Using a platinum substrate, Suhrman and Theissing[345] observed a maximum threshold greater than 6000A. for an approximately monatomic layer, and a selective maximum at ~3500A. Mayer,[346] for potassium on platinum and tungsten, obtained the maximum photoelectric yield at a thickness less than one atomic layer. The behaviour on iron substrates has been described by Brewer.[347]

Other studies have suggested that the above effects are not properties of pure potassium. For example, Mayer[348] found a continuous increase with thickness in the response of gas-free films of potassium on platinum, but a maximum was obtained for films in which gas had been deliberately introduced to about a unimolecular layer. Also, results obtained by Rentschler and Henry[349] using extremely clean sputtered metal surfaces onto which potassium was distilled suggest that the shift of the threshold to long wave-lengths for small thicknesses of potassium requires the presence of an impurity, such as oxygen, capable of reacting with the alkali metal. The theory of the effect of adsorbed potassium atoms and ions on the photoemission from metal surfaces has been discussed by de Boer and Veenemans.[350]

At −180° C. the spectral distribution curve of potassium has been found to suffer a shift to shorter wave-lengths compared with that at +20° C.[351] The shift, which was reversible and reproducible, decreased from 500A. at the long-wave limit of 6500A. to 80A. in the blue. Above −80° C. and below −100° C. the response to monochromatic light was independent of temperature, but within this narrow range it suffered a sudden change which was attributed to a phase transition. The large value of the threshold wave-length compared with that for pure potassium (5500A.) suggests some surface contamination. Ives and Johnsrud[352] using a cathode with a crystalline specular surface, prepared by slowly cooling molten potassium, found that the photoelectric emission decreased continuously from 60° C. to −180° C. The decrease was more marked with yellow light than with blue or violet light. Rough matt surfaces prepared by rapid solidification of potassium and distillation of further potassium onto the cold surface showed less temperature variation. The decrease of emission shown by the specular surfaces was attributed to an increase in work function with decrease of temperature. Other measurements[353] have shown a continuous decrease in the photoelectric emission with decreasing temperature down to 21°K., the change being much greater for red light than for blue.

Investigations have been made of the velocity distribution[354–356] and directional distribution[357] of photoelectrons from potassium surfaces.

A theory of the surface photoelectric effect in potassium has been given by Mitchell[358,359] who obtains fair agreement with experimental spectral distribution curves.

Composite Photocathodes.

When a thin (approximately monatomic) layer of potassium is separated from a metal substrate - either potassium or another metal - by a thin dielectric layer, the selective maximum can be greatly enhanced. Such composite layer surfaces may, for example, be produced by exposing a thick layer of potassium to atomic hydrogen which coats it with a thin layer of hydride onto which the final thin layer of potassium is deposited.[360,361] The atomic hydrogen for sensitization has been produced by a heated tungsten filament in hydrogen at low pressure,[362-364] and by a glow discharge in hydrogen.[339,340,361,365,366] In the latter case a trace of water vapour appears to be necessary,[340,366] and mixtures of helium and water vapour have proved as effective as moist hydrogen.[366] Because of the finite vapour pressure of potassium and the rapid surface migration of potassium ions the final potassium layer may be formed spontaneously if an excess of potassium is present.[361] Fig. 6 shows the spectral response curves for a compact potassium surface (*a*) immediately after distillation and (*b*) after the passage of a glow discharge in hydrogen.[340] The former curve is on a twenty times enlarged scale compared with the latter.

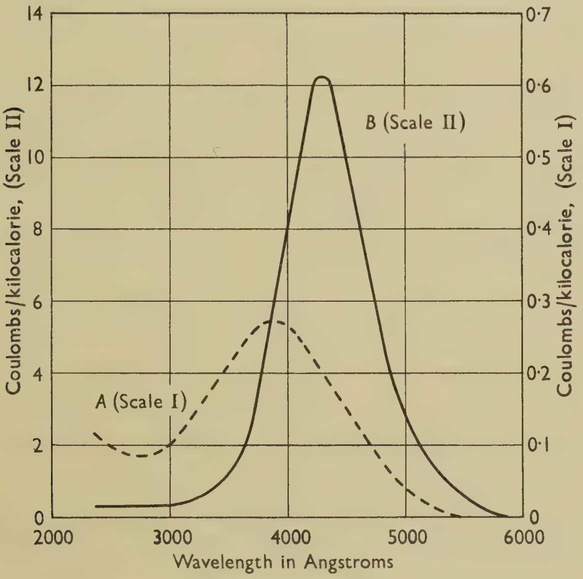

FIG. 6. SPECTRAL RESPONSE CURVES FOR A COMPACT POTASSIUM SURFACE (A) IMMEDIATELY AFTER DISTILLATION AND (B) AFTER PASSAGE OF A GLOW DISCHARGE IN HYDROGEN

The selective maximum for surfaces prepared by the above methods has been reported as 4300A.,[367] 4360A.[368,369] and 4400A.[370] Fleischer[369] obtained a maximum photoelectric yield of $37{\cdot}9 \times 10^{-2}$ coulombs per calorie of absorbed light of wave-length 4360A., which corresponds to 25•7% of absorbed photons ejecting electrons. Riyanov[362] found a maximum increase (20 to 40 fold) in sensitivity when the number of hydrogen atoms adsorbed per cm.^{2} was 3×10^{16}

– *i.e.* the same as the number of atoms per cm.^{2} in a plane potassium surface. With more than twice this amount of hydrogen the sensitivity was less than for bulk potassium, but the maximum sensitivity could be restored by heating to 60° to 70°C.

Dry molecular hydrogen which does not react with pure potassium in bulk has no effect on the photoelectric emission of a solid potassium surface,[340,370] but with a monomolecular layer of potassium on spongy platinum a covering layer of hydride forms and the photoelectric sensitivity is considerably reduced.[340] Deposition of a further layer of potassium is then necessary tc give the enhanced sensitivity.[367,368] Bosworth[360] found the photoelectric emission from a monatomic layer of potassium on tungsten to be unaffected by molecular hydrogen at temperatures up to 600°K., but when the potassium was converted into hydride by atomic hydrogen and then coated with a further film of potassium the film became very sensitive with a threshold at 8300A. An even more sensitive surface with a threshold at 9200A. was produced by covering a film of hydrogen on tungsten with potassium.[360]

Kluge and Rupp[371] made an electron reflexion study of the structure of potassium surfaces sensitized in various ways by hydrogen and found that the maximum photoelectric sensitivity corresponded to small (atomic) potassium particles embedded in or on the potassium hydride surface.

Replacing hydrogen by deuterium has resulted in no shift in the wavelength of maximum sensitivity.[372]

Composite photocathodes incorporating potassium monoxide as the dielectric layer show a similar high photoelectric sensitivity. It was found by Pohl and Pringsheim[373] in 1913 that potassium exposed to dry oxygen at a pressure of a few tenths of a mm. of mercury became coated with a coloured layer and exhibited a strong selective maximum at 4050A. The top layer of potassium presumably forms spontaneously. The maximum sensitivity for this type of composite surface occurs with 4×10^{-4}g. of oxygen per cm.^{2} of potassium.[374,375] Fleischer[376] exposed potassium to oxygen and produced a photoelectrically inactive black layer which after heating to the melting point of potassium showed a selective maximum at 3130A. It has been considered[377] that in this case there is no longer a K_2O layer but merely a few adsorbed oxygen ions. A selective maximum at 3130A. was also found by Wiedmann.[378] For a layer of K_2O topped by potassium on a silver substrate, Kluge[379] observed two selective maxima at about 4100A. and 5000A. with a threshold at 8000A. A composite surface K–Ag–K_2O–Ag has been reported to show a higher sensitivity over a wider range of wave-lengths than one without the internal silver layer: it had two selective maxima (one between 3300 and 3700A., the other at 5000A.) and to light from a gas-filled tungsten lamp (colour temperature 2700°K.) it had a sensitivity of up to 20 μamp. per lumen.[380,381]

Many other substances have been reported to bring about sensitization of potassium surfaces. For surfaces treated with sulphur, selenium and tellurium, selective maxima appear at 4100A., 4250A. and 4300A. respectively.[382] Surfaces sensitized with nitric oxide and nitrogen dioxide show strong selective maxima at 3340A. and 3650A. respectively.[383,384] An early study[385] showed pure argon and nitrogen to be without effect on the sensitivity of potassium surfaces, but in later work[383,384] nitrogen has been reported to give a selective maximum at 3650A. Carbon dioxide has been reported to give a maximum, whilst mercury was found to decrease the emission.[386] Olpin,[387,388] who investigated the effect of a wide variety of substances on potassium photocells, found that those enhancing the sensitivity included air, hydrogen, oxygen, water vapour, sulphur vapour, sulphur dioxide, hydrogen sulphide, carbon disulphide, tellurium, iodine, bromine, methyl alcohol, acetic acid, benzene, nitrobenzene, acetone, chloroform and a number of organic dyes of the type used as sensitizers in photography. Suhrmann[361,389,390] found that a thin film of naphthalene topped by potassium gave a strong selective maximum at 4200A. but that with a film of paraffin there was no selective effect. At low temperatures, cells with naphthalene[391-393] show a second maximum at a shorter wave-length, while those with anthracene[393] show several short wave-length maxima.

Sensitization of potassium surfaces by simultaneous treatment with two or more substances – for example, oxygen and hydrogen[376,394,395] or oxygen and sulphur[387] – has been described.

The general effects of low temperatures on surfaces of the type: alkali metal–intermediate layer–alkali metal is to cause a displacement of the spectral maximum to a shorter wave-length.[393]

Spectral characteristics of potassium–antimony photocathodes have been studied[395a-d] (cf. page 2311).

Effect of Electric Fields.

Electric accelerating fields reduce the work function of potassium surfaces,[396,398] the photoelectric threshold for pure potassium shifting from 5620A. to 5880A. in a field of 36 kV./cm.[397] If a layer of oxygen separates a potassium film from a tungsten substrate the effect of the field depends on the thickness of the oxygen layer. For an approximately monatomic oxygen layer a threshold shift from 5830A. to 5960A. was produced by a field of 18·6 kV./cm., whilst with a thicker oxygen layer this field caused a shift from 7350A. to 7575A.[397] For very thick oxygen layers the threshold is independent of field strength but the emission increases with increasing field strength.

Photoionization.

Photoionization of potassium vapour occurs at wave-lengths above and below the spectral series limit of 2856·6A. (*i.e.* the wave-length corresponding to the ionization potential). Ditchburn, Turnstead and Yates,[399] who measured the absorption coefficient of potassium vapour by photographic spectrometry, found that the atomic absorption cross section of potassium increased with decreasing wave-length from at least 3100A. to a peak ($1{\cdot}2 \pm 0{\cdot}3 \times 10^{-20}$ cm.^{2}) near the series limit. It then decreased to a minimum at 2700A. before increasing steeply at least as far as 1700A. where it was about twenty times its value at the series limit. The absorption is entirely attributable to photoionization. Earlier measurements[400] using a space charge detector gave similar results down to 2300A., but showed a maximum at this wave-length. Ditchburn *et al.*[399] suggest that the maximum at 2300A. was due to a neglected complication of the space charge detector.

Other earlier studies of photoionization in potassium vapour were made by a number of authors.[401-408] The first measurements were made by Williamson[401,402] who observed that the formation of positive ions began between 2800A. and 3100A. and he presumed that it actually started at the spectral series limit (2856A.). His subsequent work[406] showed that there was ionization at longer wave-lengths than the series limit. It was at one time thought[404,406,407] that potassium molecules were responsible for the observed dependence of the ionization on wave-length but it was later realized[400] to be an atomic property.

Bates[409] has investigated the photoionization of atomic potassium by quantal methods and has shown that the general features of the observed behaviour can be understood. The calculations have been taken further by Seaton:[409a] an earlier treatment[410] was less successful.

Studies of the angular distribution of photoelectrons ejected from potassium vapour illuminated by polarized ultra-violet light have shown the most probable direction of ejection to be that of the electric vector.[411-415] The distribution varies as the square of the cosine of the angle between the electric vector and the direction in question.

The molecular absorption cross section of potassium shows a broad minimum of about 10^{-18}cm.^{2} between 3100A. and 2000A.[399] It rises sharply outside these limits.

Radioactivity

The natural radioactivity of potassium has long been known (Mellor, II, 467), but it was not until 1928 that the emission of γ-radiation in addition to β-radiation was discovered.[416] The absorption coefficient of the γ-radiation in lead is about 0·6cm.$^{-1}$.[417-419] Bocciarelli[420,421] in 1932 reported that the radiation from potassium had three components: a soft β-component with a velocity of about 0·83*c* (*c* = velocity of light), a harder β-component with a velocity about 0·93*c*, and a very hard γ-component. Potassium has a lower β-ray activity than rubidium[417,422] but the emission from potassium has a much greater penetrating power.[423-425] The source of the radioactivity is the isotope ^{40}K which occurs in natural potassium to the extent of about 0·01%. Until the mid-1930's, however, the radioactivity was attributed to ^{41}K. This subject is discussed in more detail on page 1555.

Miscellaneous Physical Properties

The chemical constant of potassium has been discussed by several authors.[111,117,426-430a] Edmondson and Egerton[430] gave it a value of 0·92 ± 0·04, while Newmann and Völker[111] gave 1·105 ± 0·05. Other more recent calculations have given 1·126 ± 0·1.[430a]

Ultrasonic waves of frequency 12Mc./sec. have a velocity of 1820 ± 20 m./sec. in liquid potassium at its melting point.[67] Between the melting point and 160°C. the temperature coefficient is $-0{\cdot}5$m.sec.$^{-1}$degree^{-1}.

From the anomalous rise of electrical resistance that starts well below the melting point the activation energy for self-diffusion in potassium has been estimated as 9·1 ± 0·1 kg.-cal./mole.[430b,c]

By the use of the Stokes–Einstein equation, the coefficient of diffusion of potassium in mercury at 8° to 15°C. has been calculated from the atomic radius and viscosity data to be 0·48cm.^{2} per 24 hours,[431] which is in reasonable agreement with the older experimental value (Mellor, II, 456) of 0·53cm.^{2} per 24 hours at 10·5°C.

When alkali halide crystals are heated in contact with an alkali metal in the liquid or vapour state, the crystals acquire a stoicheiometric excess of alkali metal and assume a deep colour.[431a-c] The absorption band (F-band) giving rise to the coloration has a maximum in or near the visible region of the spectrum and the actual colour is characteristic of the crystal and not of the alkali metal. The absorbing centres responsible for the F-band are known as Farbzentren or F-centres[431a-c] (see page 2526). In deeply coloured crystals the excess alkali metal may be present to the extent of about 1 part in 10^3 to 10^4. Potassium chloride and other crystals additively coloured with potassium have been prepared by a number of workers[431d-m] who have studied such properties as their absorption spectra, photoconductivity and magnetic resonance. The rate of penetration of coloration into potassium chloride in contact with liquid potassium has been measured as 2·03mm./hr. at 700°, 0·87 mm./hr. at 600°, and 0·48mm./hr. at 500°.[431f] Layers with very high colour-centre concentrations have been produced by evaporating in vacuo both alkali halides and free alkali metal and condensing the vapour on a cold plate.[431g] Coloration of alkali halide crystals also occurs when they are exposed to *X*-rays, electron bombardment, or pile irradiation.[431a-c,n]

Studer and Williams[432] obtained $-0{\cdot}0042$ for the Hall constant of potassium. More recently, Justi[154] obtained $-0{\cdot}00350$ at room temperature and $-0{\cdot}00352$ at

20·4°K. Theoretical calculations of the Hall constant have given[432] -0·004715 and -0·00476.[434]

From electrode potential measurements on amalgam systems, Klein and Lange[435] obtained electron work functions for a larger number of metals, their value for potassium being 1·60e.V.

Direct determinations of the dielectric constant, ϵ, of potassium vapour have been made at 500°C. for pressures of 10 to 100mm.Hg, the value at 10 mm.Hg being 1·000920.[436] At low pressures $\epsilon - 1$ is directly proportional to the pressure, and by assuming that this proportionality holds up to atmospheric pressure a value of 1·19 is obtained for the dielectric constant of potassium vapour at one atmosphere and 0°C.

Scattering of a beam of potassium atoms has been studied in a number of gases.[437]

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PROPERTIES OF THE POTASSIUM ION

Some properties of the potassium ion, and some properties that relate to both the metal and its ion, have been dealt with under the appropriate sections above. Other properties of the K^+ ion will be considered here.

The Ion in Solution.

At 25°C. the heat and free energy of formation of the aqueous potassium ion are −60·04 and −67·466 kg.-cal./g.-ion respectively.[1] The absolute heat capacity of the K^+ ion at infinite dilution has been calculated from measurements in various aqueous salt solutions.[1a,b] Assuming equal values for the heat capacities of the NH_4^+ and Cl^- ions, that of the Na^+ ion has been given as −21·6 g.-cal./degree/g.-ion.[1a] From thermal data for the two ionization processes KCl(solid) → K^+(aq.) + Cl^-(aq.) and KBr(solid) → K^+(aq.) + Br^-(aq.) a mean value of 24·2 ± 0·2 g.-cal./g.-ion/degree has been obtained for the entropy of the K^+ ion (relative to that of the H^+ ion) in aqueous solution at 25° C.: values from the individual processes were 24·2 ± 0·2 and 24·3 ± 0·8 respectively.[2] The U.S. Bureau of Standards selected value[1] for the entropy of the aqueous potassium ion at 25° C. is 24·5 g.-cal./g.-ion/degree.

After calculating the effective diameter of the hydrated potassium ion by a variety of methods, Kielland[3] took a rounded value of 3×10^{-8} cm. for this dimension and then used the Debye–Hückel theory to compute the values of activity coefficient for the potassium ion in aqueous solution at 25° that are shown in Table XV.

TABLE XV. - ACTIVITY COEFFICIENTS OF THE K^+ ION IN AQUEOUS SOLUTION AT 25° C.

Total ionic concentration	0·001	0·002	0·005	0·01	0·02	0·05	0·1	0·2
Activity coefficient	0·975	0·964	0·945	0·925	0·899	0·85	0·805	0·755

The indefinite significance of ionic solvation numbers has been discussed by Bockris[4] who has distinguished between primary and secondary solvation (see page 56). Even when using methods considered to give a measure of the primary solvation - viz. methods employing ionic mobility, ionic entropy, compressibility and partial molar volume - the resulting values for the K^+ ion show considerable variation. Thus, the methods mentioned above have yielded values of 4, 2, 3 and 0 respectively.[4] In the case of the first of these, the value was extrapolated to aqueous solutions from results in alcoholic solutions.

Independent treatments by Latimer and co-workers[5] and by Verwey[6] have led respectively to values of 75·8 and 75 kg.-cal.g.-ion^{-1} for the heat of hydration of the potassium ion, to 73·5 and 72 kg.-cal.g.-ion^{-1} for the free energy of hydration, and to 8 and 11·0 g.-cal.g.-ion^{-1}degree^{-1} for the entropy of hydration. Earlier, Bernal and Fowler[7] made use of two methods to calculate values of 94 and 92 kg.-cal.g.-ion^{-1} for the heat of hydration of the K^+ ion. A calculation by Webb[8] gave 81·9 kg.-cal.g.-ion^{-1} for the free energy of hydration. Rather than follow Bernal and Fowler's[7] basic assumption of equal heats of hydration for the equi-radial K^+ and I^- ions, Miscenko,[8a] in separating the heats of hydration of salts into values for the individual ions, has ascribed equal heats of hydration to the Cs^+ and I^- ions on the grounds that the difference in their radii is compensated by the dipole moment asymmetry in the water molecule. By this means he obtained 80 kg.-cal.g.-ion^{-1} for the heat of solvation of the K^+ ion. In an earlier paper, Miscenko,[9] again using thermochemical data on the solvation of salts, gave the heat of solvation of the K^+ ion in water as 78 kg.-cal.g.-ion^{-1}, and in ethyl alcohol as 79 kg.-cal.g.-ion^{-1}. From the Bjerrum equation for solvation the same author[9] calculated values of 124, 126 and 128 kg.-cal.g.-ion^{-1} for the heat of solvation of the K^+ ion in water, methyl alcohol and ethyl alcohol respectively: from the Born equation for solvation he calculated 122, 120 and 119 kg.-cal.g.-ion^{-1} for the solvation energies in the same three solvents. A number of dubious assumptions are, however, involved in these calculations.[10]

A recent compilation[11] of ionic mobilities gives the values in Table XVI for the equivalent conductivity or mobility of the potassium ion at infinite dilution in water.

The value at 100° C. is said to be reliable only within several units, while the values at 5°, 15°, 25°, 35° and 45° C. are reliable to within the last figure given, and those at 0° C. and 18° C. to within two or three units in the last figure given. In deuterium oxide at 25° C. the mobility of the potassium ion at

TABLE XVI.- MOBILITY OF THE POTASSIUM ION AT INFINITE DILUTION IN WATER

Temp., °C.	0	5	15	18	25	35	45	55	100
λ_∞	40·7	$46{\cdot}7_5$	$59{\cdot}6_6$	63·9	73·50	$88{\cdot}2_1$	$103{\cdot}4_9$	$119{\cdot}2_9$	195

infinite dilution is 61·23:[12] at 18°C. it is 54·5.[12a] In methyl alcohol the mobility at infinite dilution has been given as[13] 53·6 and[14] 52·40 at 25°C. and as[13] 39·35 at 4°C., while in ethyl alcohol[13] it is 20·85 at 25°C. and 13·53 at 4°C. There is a substantial body of data for the conductivity of potassium salts in other non-aqueous solvents but few transport number data corresponding to them. Mobilities of the potassium ion in a range of non-aqueous solvents have been deduced,[15,16] however, by the use of such relationships as that between conductivity and viscosity (Walden's rule). The heat of transport[17] and entropy of transport[18] of the K^+ ion have been studied.

By the use of Nernst's limiting formula $D^\circ = RT\lambda_\infty/zF^2$ diffusion coefficients at infinite dilution may be calculated from the above mobility data. In this way a value of $1{\cdot}96 \times 10^{-5}$ cm.^{2}sec.$^{-1}$ is obtained for the self-diffusion coefficient of the potassium ion at infinite dilution in water at 25°C. Self-diffusion coefficients for the K^+ ion in aqueous solutions of potassium iodide[19] and potassium chloride[19a] at 25°C. have been determined by means of the open-ended capillary tube method using ^{42}K as radio-tracer (Tables XVII and XVIII).

TABLE XVII.- SELF-DIFFUSION COEFFICIENTS OF K^+ IN KI(AQ.) AT 25°C.

K^+ concentration g.-ion/litre	$D \times 10^5$ cm.^{2}/sec.
0·05	1·970
0·10	2·005 ± 0·030
0·29	2·060 ± 0·040
0·50	2·030 ± 0·030
0·774	2·080 ± 0·050
1·000	2·030 ± 0·040
1·96	1·910 ± 0·050
3·062	1·850 ± 0·060

TABLE XVIII.- SELF-DIFFUSION COEFFICIENTS OF K^+ IN KCl(AQ.) AT 25°C.

K^+ concentration g.-ion/litre	$D \times 10^5$ cm.^{2}/sec.
0·040	1·890 ± 0·01
0·100	1·87 ± 0·029
0·250	2·033 ± 0·034
0·500	2·135 ± 0·004
1·000	2·113 ± 0·040
2·000	2·013 ± 0·040
3·000	1·903 ± 0·010

The maximum in the diffusion coefficient/ionic concentration curve has been explained[19b] by ascribing the rise to disorder in the solvent and the decrease from the maximum to ion dipole interaction. Another possible explanation is that the degree of hydration of the potassium ion changes with concentration.[19a]

The specific viscosity of the K^+ ion in 0·1N. aqueous solution has been calculated as −0·0030.[20]

Values[21] for the magnetorotary power of the potassium ion (in min.cm.^{2} gauss^{-1}g.-ion^{-1}) resulting from the work of Okazaki on the Faraday effect in aqueous salt solutions are as follows; the value for the hydrogen ion is taken

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as zero:-

Wave-length, A.	5900	5500	5100	4700	4300	3900	3500
[M.]	0·24	0·26	0·33	0·39	0·50	0·64	0·77

The contribution of the potassium ion to Okazaki's molecular magnetorotation constant, Φ, (see page 422) is $0{\cdot}61 \times 10^{-14}$.[22]

The refractivity of the potassium ion in aqueous solution for the sodium *D*-line is 2·23.[23]

Exchange of K^+ ions with other ions has been studied using many of the cationic exchange resins that have been developed during recent years.[23a-z, 24-24d] It has also been studied in soils, clays and minerals.[25-25t] Most attention has been paid to the system K–H[23f,g,m,o,q-t,y,24d] but other systems to have received attention include K–Na,[23l,o,25j] K–Li,[23o,r] K–NH_4,[23c-e,p,s] K–Tl,[25j] K–Ag,[25n,t] K–Cu,[25c] K–Ca,[25r,s] K–Ba,[23w] K–Mg.[24] For ions of equal charge the strength of binding of an ion by an exchanger increases with decreasing hydrated radius, and in dilute solutions the adsorption or exchange affinities of alkali metal ions follow the series $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$.[23a,c,25] Ion exchange is better dealt with from the viewpoint of the exchanger than from that of the individual ion and so will receive no detailed treatment here: there are a number of specialist books that may be consulted for further information on ion exchange and its applications.[25u-x]

The Gaseous Ion.

Various ion sources for gaseous K^+ ions have been described, a widely used method of production being to heat certain potassium compounds.[24-35] Potassium aluminium silicates[29,32,34,35] e.g.[29] $3K_2O, Al_2O_3, 2SiO_2$ and mixtures of iron oxide and a potassium salt[24-27,30,31,33] (Kunsman catalysts) have been used for this purpose. In another method, potassium atoms obtained by vaporization of the metal are ionized when they impinge on a hot tungsten or platinum filament.[36-38] Using either method the resulting ions may be accelerated to the required potential in an electric field. A typical ion emission intensity is of the order of 10^{-4} amp./cm.^{2}.[29,30,37] Potassium ions can also be produced by the use of high-speed charged particles or short wave-length radiations (see also pages 1523 and 1529).

The heat of formation of the gaseous potassium ion is 121·81 kg.-cal.g.-ion^{-1} at 0°K. and 123·07 kg.-cal.g.-ion^{-1} at 298·16°K.[1]

At 20°C. and a pressure of one atmosphere the mobility of the K^+ ion (in cm./sec./volt/cm.) in various gases is as follows:-[39,40]

Helium	22·3
Neon	7·88
Argon	2·77
Krypton	1·98
Xenon	1·50
Hydrogen	13·5
Nitrogen	2·70

Other measurements[41,41a] agree well with the above. The temperature variation of the mobility in argon has been studied between 78° and 460°K.,[42] and mobility measurements have also been made in argon–xenon mixtures.[43] In the presence of water vapour, alkali metal ions acquire a cluster of water molecules which reduces their mobility. The mobility of the K^+ ion has been studied in helium, neon, argon and xenon containing small concentrations of water vapour, and the reduction in mobility amounts to 20% to 50%.[41] In argon and xenon an upper limit of six has been assigned to the number of water molecules in an ion cluster, but the actual number is probably less. Measurements have also been made in pure water vapour,[44] and the mobility of K^+ ions in the Bunsen flame has been studied.[45]

A considerable amount of work has been done on ionization of the inert gases by potassium ions.[26,31,32,46-60] Beeck and Mouzon[50-52] reported that, in general, an inert gas was most easily ionized by the ions of the alkali metal nearest to it in the Periodic Table, and the potentials (ion velocities) required by K^+ ions to ionize neon, argon, krypton and xenon were given as 320, 95, 80 and 120V. respectively. It has, however, been suggested[31,56] that in these measurements there was some interference from secondary electrons. In later investigations, Varney,[31] using a space-charge method sensitive to any resulting positive ions but unaffected by secondary electrons from the walls, obtained values of 82, 69 and 114V. for the potentials required for ionization of argon, krypton and xenon respectively. No ionization of helium by K^+ ions with potentials up to 500V. was found by Varney,[31] but other workers have reported ionization at considerably lower potentials. Davies[32] reported that ionization of helium by K^+ ions began at an accelerating potential of about 450V., whilst Frische[55] obtained a potential less than 400V. and Sutton and Mouzon[46] gave 150 to 200V.

Several studies have been made of the scattering of potassium ions in mercury vapour and of the ionization of mercury vapour by potassium ions.[54,55,60-64] Frische[54,55] reported no ionization of mercury vapour below 250V. but found that above 250-350V. the ionization increased with increasing potential. In other work, Varney *et al.*[60] reported no ionization up to 300V.

Ionization of other gases such as nitrogen,[31,55,59] hydrogen,[55,66] carbon monoxide[55] and carbon dioxide[59] by potassium ions has also been studied. Schmidt[61a-d] studied the scattering and loss of velocity of 25V. and 200V. potassium ions in a number of gases and vapours including carbon monoxide, carbon dioxide, methyl chloride, methane, ethane, *iso*butane, ethylene, *iso*butylene, acetylene, butadiene and ammonia, as well as nitrogen, hydrogen, oxygen and the rare gases.

Reflexion of potassium ions and emission of electrons on bombarding both solid and liquid metal surfaces with potassium ions has been studied.[66a-e]

By applying an electric field between an anode in potassium vapour and a cathode placed on the other side of a glass diaphragm enclosing the vapour, potassium ions may be carried from the gas phase into the glass.[66] Warburg and Tegetmeier[66g] in 1888 found that lithium and sodium ions under the influence of an electric field would migrate through quartz plates in a direction parallel to the principal crystallographic axis, but that potassium ions under similar conditions would not. It has been suggested[66h] that lithium and sodium ions are small enough to pass through tunnels in the quartz while potassium ions are too large. Migration of potassium ions through quartz plates in the direction of the principal axis has since been observed, but the oxygen framework of the quartz undergoes distortion.[66i]

The ionic refractivity of the free potassium ion for the sodium *D*-line is 2·23.[23] Values for the polarizability of the potassium ion include $0{\cdot}80 \times 10^{-24}$,[67] $0{\cdot}84 \times 10^{-24}$,[68] $0{\cdot}87 \times 10^{-24} \pm 0{\cdot}02 \times 10^{-24}$,[69] and $0{\cdot}88 \times 10^{-24}$.[23] Other dielectric parameters of the potassium ion have been evaluated.[70-72]

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SOLUTIONS OF POTASSIUM AND SOLUBILITIES IN POTASSIUM

Solutions of Potassium in Liquid Ammonia

Potassium dissolves in liquid ammonia to give solutions having a blue colour when dilute and a metallic copper-like appearance when concentrated.[1] The absorption spectrum of dilute solutions shows a single broad absorption band with a maximum around 6700cm.$^{-1}$ and a width at half-height of about 3000cm.$^{-1}$.[1a] Solutions of maximum stability may be prepared by the technique described for sodium[2] (see page 427). Decomposition of the solutions is catalyzed by even minute traces of impurities. The solubility of potassium in liquid ammonia increases slightly with increase of temperature; the composition of saturated solutions expressed in g.-moles of ammonia per g.-atom of potassium is 4·68 at 0°C., 4·95 at -33·5°C. and 5·05 at -50·38°C.[3] Over a wide range of concentrations the heat of solution is virtually zero.[4,5]

A study of the phase diagram for the system potassium-ammonia at temperatures below the freezing point of ammonia (-78°C.) has shown the presence of a eutectic at about 15 mole-% potassium, the eutectic temperature being −157° C.[6,7] The solid is a mixture of ammonia and silvery potassium crystals: ammoniates are not formed in this system. There is some doubt whether or not separation into two liquid phases occurs at temperatures a little above −78° C.[7] Ogg[8] has reported that on cooling very dilute solutions (10^{-4} to 10^{-3} M.) of potassium in ammonia to temperatures down to −180° C. a single homogeneous crystalline phase separates out. This has a blue colour visually identical with that of the corresponding liquid phase.

Potassium adsorbed on films of solid ammonia at −183° C. and at a pressure of 10^{-3} to 10^{-4}mm. Hg shows the same coloration and optical absorption as in solutions.[9] A light absorption band at 1·15u is observed in thin layers of ammonia containing small amounts of potassium, sodium or lithium at 20° K.[9a] In addition there are bands characteristic of the actual alkali metal employed.

The density of solutions of potassium in liquid ammonia is less than that of either of the constituents. Density values at −33·2° C. are given in Table XIX[10] (density NH_3 at −33·2° C. = 0·6816).

TABLE XIX. - DENSITY OF SOLUTIONS OF POTASSIUM IN LIQUID AMMONIA AT −33·2° C.

Moles NH_3/Atom K	4·95 (satd.)	7·03	9·65	11·20	13·20
Density	0·6282	0·6351	0·6433	0·6483	0·6522
Moles NH_3/Atom K	17·75	23·18	26·76	30·64	34·08
Density	0·6598	0·6659	0·6685	0·6701	0·6721

The volume expansion on solution has a maximum value of 29·80 c.c. per g.-atom of potassium for a solution containing about 10·5 g.-moles of ammonia to each g.-atom of potassium; for a saturated solution it is 27·28 c.c. per g.-atom of potassium. Saturated solutions have densities varying from 0·628 at −32·2° C. to 0·638 at −49·6° C.[11]

Fig. 7 shows the vapour pressure behaviour of solutions of potassium in ammonia at −50·38° C., −33·5° C. and 0° C.[3] The horizontal portion of each curve corresponds to a region where excess solid potassium is present, the sudden rise in vapour pressure commencing at the saturation composition. The vapour pressures of the saturated solutions at the above three temperatures are 63, 162 and 760 mm. Hg respectively. In view of the smooth form of the curves there would appear to be no compound formation between potassium and ammonia.

Dilute solutions of potassium in ammonia show an electrical conductivity behaviour similar to that of ordinary electrolytes, the equivalent conductivity (specific conductivity × dilution) approaching a limiting value with increasing dilution. At a concentration of ~0·04M. there is a minimum equivalent conductivity, and in more concentrated solutions the equivalent conductivity increases rapidly with increasing concentration. Fig. 8 shows the equivalent conductivity curve at −33·5° C. resulting from the measurements of Kraus[12] in which the 'dilution', V, was given as the number of litres of pure solvent containing one gram atom of potassium, and the equivalent conductivity, Λ, was given as 1000V × specific conductivity.

Other measurements by Gibson and Phipps[13] at −33·5° C. and −48·5° C. show the same behaviour. In very dilute solutions (~0·001N.) the equivalent conductivity is depressed - probably by several percent - because of some reaction of potassium with ammonia to form amide.[12,13] In concentrated solutions the conductivity is metallic in character, the specific conductivity of a saturated solution of potassium in ammonia at −33·5° C. being approximately half that of mercury at 0° C.[14] Table XX contains values for the specific

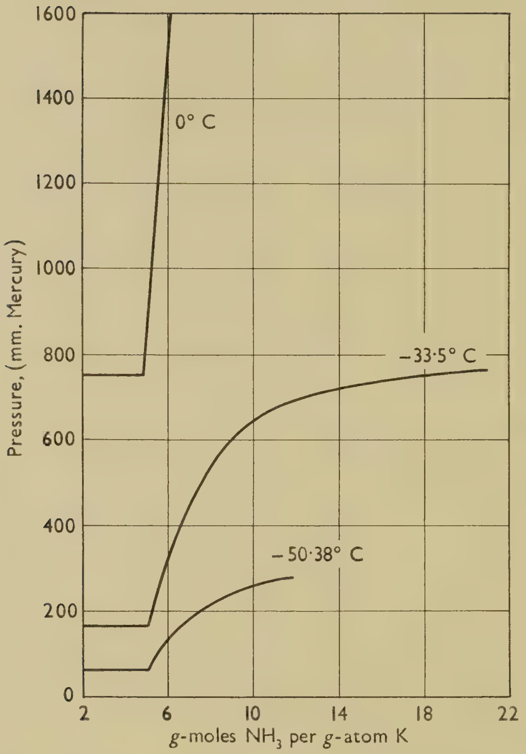

FIG. 7. VAPOUR PRESSURE OF SOLUTIONS OF POTASSIUM IN LIQUID AMMONIA

TABLE XX. - SPECIFIC CONDUCTIVITY OF CONCENTRATED SOLUTIONS OF POTASSIUM IN AMMONIA AT −33·5°C.

V, litres NH_3/g.-atom K	0·0853	0·1295	0·1730	0·2466	0·3205	0·4031
κ, $ohm^{-1}cm.^{-1}$	4569	4190	2511	1278	692·8	359·2
V, litres NH_3/g.-atom K	0·4881	0·5782	0·7310	0·8893	1·240	1·597
κ, $ohm^{-1}cm.^{-1}$	174·4	78·65	19·95	6·279	1·415	0·7470

conductivity, κ, of concentrated solutions.[14,15]

The resistance-temperature coefficient, $1/R_{-33\cdot5}\frac{\Delta R}{\Delta T} \times 100$, increases from 0·0438% per degree for a saturated solution to a maximum of 4·55% per degree at a dilution of about 0·91 litres.[15] It then falls to about 1·5% per degree for dilutions above 4 litres. The temperature coefficient increases as the temperature decreases and the percentage change of the coefficient is greater at higher concentrations.[15] The coefficient d $\ln\kappa/dT$, which has a value of 0·029 for dilute solutions (V = 25 to 250 litres), is practically independent of temperature.[13]

Conductivities of sodium and potassium in dilute ammonia solutions are substantially additive, there being no evidence of compound formation between the metals.[12,16]

Kraus[12,17] has accounted for the observed conductivity behaviour in ammonia solutions of potassium by his solvated electron theory (see page 429)

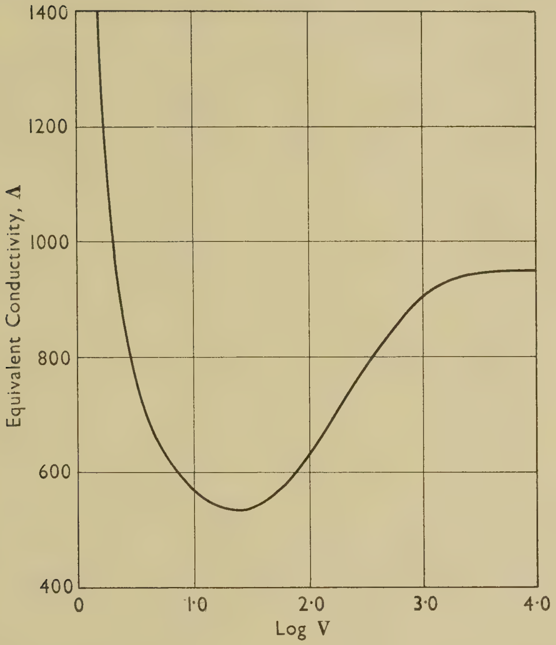

FIG. 8. -EQUIVALENT CONDUCTIVITY OF AMMONIA SOLUTIONS OF POTASSIUM AS A FUNCTION OF DILUTION (33·5°C.)

according to which potassium atoms, potassium ions, free electrons and solvated electrons are in equilibrium in ammonia solutions:-

$$K \rightleftharpoons K^+ + e^-$$
$$e^- + nNH_3 \rightleftharpoons e^-(NH_3)_n$$

More recently it has been suggested that the electrons are trapped in the solvent, there being in the liquid cavities which serve to trap electrons singly or in pairs.[18-18b] A number of authors[1a,18c-g] have discussed and elaborated this model which is compatible with a large body of experimental data.

Ogg[8] found that solid solutions prepared by cooling very dilute solutions of potassium in ammonia were good electrical conductors and that they had a positive temperature coefficient of resistance in contrast to the negative coefficient for liquid solutions (cf. sodium, page 430).

The thermoelectric properties of potassium solutions in liquid ammonia at -33° C. have been studied over the concentration range 0·002M. to saturation.[1] Throughout the range there is a decrease in thermoelectric power with increasing potassium concentration, approximate values being 750μ volts/°C. at 0·003M., 250μ volts/°C. at 0·1M., 50μ volts/°C. at 1·0M. and 1·5μ volts/°C. at 10M.

Table XXI shows the results of measurements of the magnetic susceptibility of potassium dissolved in ammonia at -33° C. and -53° C.[18] The second column gives values for the specific volume susceptibility of the solution minus that of the solvent, while the third column gives the atomic susceptibility.

Paramagnetic resonance absorption in solutions of potassium in liquid ammonia was first observed by Hutchison and Pastor[19] at microwave frequencies.

TABLE XXI. - MAGNETIC SUSCEPTIBILITY OF POTASSIUM IN AMMONIA

Potassium concn. g.-atom/litre	κsoln. − $\kappa NH_3 \times 10^6$	$\chi_A \times 10^6$
	−33°C.	
0·00341	0·00432	1268
0·00384	0·00452	1180
0·00406	0·00505	1240
0·00481	0·00570	1180
0·00812	0·00790	974
0·00960	0·00819	853
0·0318	0·01280	402
0·482	0·0390	29·9
	−53°C.	
0·00354	0·00286	809
0·00422	0·00332	790
0·00501	0·00417	834
0·00844	0·00411	488
0·0331	0·00765	232
0·500	0·0194	−7·7

At a frequency of 23,700 Mc. the spectroscopic splitting factor (g-factor) was 2·0012 ± 0·0002. Several studies of paramagnetic resonance absorption have since been made at lower frequencies and over a wide range of potassium concentrations.[18f,19a,b] The resonance is extremely sharp and has one of the smallest widths (a few tens of milligauss) of any paramagnetic resonance absorption. Magnetic susceptibilities for static fields calculated from the radio-frequency data have shown the same pattern of concentration dependence as found in static experiments but the static measurements have given appreciably higher values.[18f,19a,b]

The solubility curve for mixtures of potassium and sodium in ammonia shows three branches corresponding to the solubility of pure potassium, of the compound Na_2K, and of pure sodium.[16] Solutions of potassium iodide in ammonia are miscible with dilute solutions of potassium in ammonia but not with concentrated solutions.[20]

Several useful reviews of the properties and constitution of metal-ammonia solutions have appeared.[21-24]

Decomposition of potassium–ammonia solutions and reactions of potassium dissolved in ammonia are discussed under 'Chemical Properties'. (page 1559).

Miscibility of Potassium and its Salts

Potassium metal and its fused halides exhibit reciprocal solubility and at high temperatures there is complete miscibility.[25,26,26a] Fig. 9 shows the phase diagram for the system potassium–potassium chloride.[26a]

Complete miscibility occurs in this case at temperatures above 790°C. – a temperature only 18°C. above the melting point of the salt. Similar curves have been given for the other potassium–potassium halide systems, complete miscibility of metal and salt occurring at temperatures above 904°, 728° and 717°C. in the cases of fluoride, bromide and iodide respectively.[26a] Consolute compositions for the fluoride, chloride, bromide and iodide systems are 20, 39, 44 and 50 mole-% metal respectively; the respective eutectic temperatures being 849°, 751·5°, 708° and 658·5°C.[26a] The temperature interval for the co-existence of two liquid phases decreases in passing from the fluoride to the bromide and then increases to the iodide.[26a]

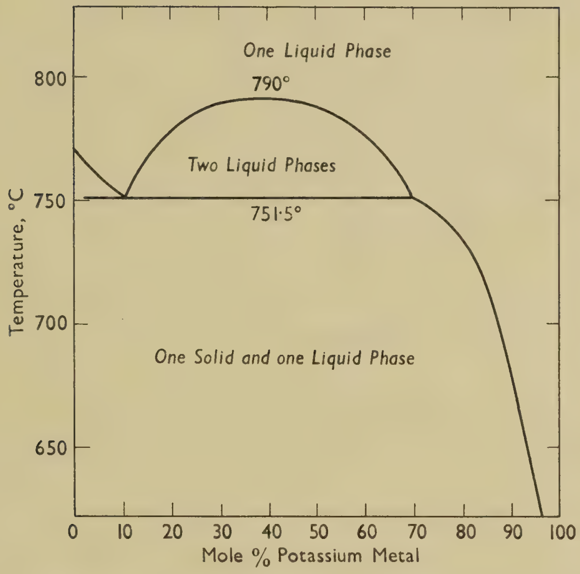

FIG. 9. THE POTASSIUM CHLORIDE-POTASSIUM METAL SYSTEM

Vapour pressure measurements on solutions of potassium fluoride in liquid potassium have been made in the pressure range 1–2 atmospheres, and the progressive lowering in vapour pressure on increasing the percentage of salt demonstrates the true nature of the solutions and shows that they are not colloidal suspensions or dispersions.[25]

The electrical conductivity of solutions of potassium in potassium chloride has been measured at temperatures above the consolute temperature of the system.[26b] Specific conductance increased continuously with the metal concentration whilst the equivalent conductance increased continuously from 3000 ohm^{-1}cm.^{2} at infinite dilution to 38,000 ohm^{-1}cm.^{2} at the maximum concentration studied (19 mole-% of potassium).

Additive coloration of alkali halide crystals by contact with liquid or gaseous potassium is discussed on pages 1672 and 2526).

Other Solutions of Potassium

Potassium is soluble in methylamine[1a,13,27,28] and in ethylenediamine.[29] An approximate figure of 1·9 × 10^{-3} moles/litre has been obtained for the solubility in methylamine at −80° C.[1a] Gibson and Phipps,[13] from electrical conductivity measurements, reported the existence of two liquid phases in the systems potassium/methylamine at −33·5° C. for potassium concentrations above about 0·01M. Kraus[29] reported that potassium was insoluble in ethylamine and in secondary and tertiary amines but other workers[1a] have claimed some solubility in ethylamine. The absorption spectrum of potassium in methylamine shows two bands at about 15,000 cm.$^{-1}$ and 12,000 cm.$^{-1}$ whilst that in ethylamine has a single maximum in the region of 15,000 cm.$^{-1}$.[1a] Electrical conductivity of solutions of potassium in methylamine are shown in Table XXII, V being the dilution in litres per g.-atom.[13]

Solubilities in Potassium

Over the range 65° to 310° C. the solubility of potassium monoxide in liquid

TABLE XXII.- EQUIVALENT CONDUCTIVITY OF SOLUTIONS OF POTASSIUM IN METHYLAMINE

−48·5°C.		−33·5°C.	
Log V	Λ	Log V	Λ
2·088	47·9	2·143	66·4
2·534	63·6	2·586	87·7
2·977	82·6	3·030	109·4
3·424	103·6	3·476	130·7
3·868	125·1		

potassium has been represented by the equation:-[30]

$$\text{Wt.-\% } O_2 = 0\cdot0865 - 0\cdot0006089t + 0\cdot00000714t^2 \ (t \text{ in } {}^\circ\text{C.}).$$

This corresponds to 0·1 wt.-% oxygen at 100°C. and 0·55 wt.-% oxygen at 300°C. The solubility of sodium monoxide in liquid potassium is much less than that of potassium monoxide. Between 50° and 360°C. the solubility of sodium monoxide in potassium and in sodium–potassium alloys may be expressed by:-[30]

$$\text{Wt.-\% } O_2 = 0\cdot0012 - 0\cdot00000871t + 0\cdot000000128t^2 \ (t \text{ in } {}^\circ\text{C.}).$$

Potassium metal may be freed from its oxide either by distillation or by reaction with a quantity of sodium equivalent to its oxide content and subsequent filtration.[30]

The solubility of potassium halides in liquid potassium has been dealt with above.

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ATOMIC WEIGHT AND ISOTOPES

Determinations of the atomic weight of potassium have, in general, followed closely the classical methods of Richards, silver being used as the standard of comparison. The most widely used method has been to prepare the chloride for weighing by fusion under air or nitrogen containing some hydrogen chloride after first purifying the starting potassium salt by crystallization as the nitrate, oxalate, chlorate, chloride, etc. The weighed potassium chloride is used to precipitate silver chloride, and the quantity of silver required for this is measured and/or the silver chloride collected quantitatively. Several workers have also made determinations of the atomic weight by precipitation of silver bromide.

Using the above methods, Hönigschmid and Goubeau[1] in 1927 obtained an atomic weight of 39·104 from the KCl:Ag and KCl:AgCl ratios; the same value also resulted from determinations of the ratios KNO_3:KCl[2] and KBr:AgBr.[3] This value was appreciably higher than that of 39·096 which is obtained when the older KCl:Ag, KCl:AgCl, KBr:Ag and KBr:AgBr ratios of Richards and collaborators[4,5] are taken together with the now accepted value for the atomic weight of silver (Ag:107·880). In 1933, Baxter and MacNevin,[6] using potassium salts from various sources and purifying them by crystallizing the nitrate, chlorate, perchlorate or oxalate, obtained K = 39·094. After a further extensive series of measurements on the KCl:Ag, KCl:AgCl, KBr:Ag and KBr:AgBr ratios, Hönigschmid and Sachtleben[7] in the same year gave support to the lower value by obtaining as their average value K = 39·096. Their potassium chloride was prepared after crystallization of the nitrate, oxalate or tartrate: the potassium bromide was prepared by the action of bromine on the oxalate. A small number of their samples gave a higher value of K = 39·104 owing, in the opinion of the investigators, to the presence of nitrate or some other ion in the fused silver chloride.

Johnson,[8] in 1935, prepared samples of potassium chloride from various sources and by applying his 'standard solution' method obtained K = 39·100. His technique was to add the dissolved chloride dropwise to a 0·2N. solution of an equivalent amount of silver, or, alternatively, to add the two solutions simultaneously and dropwise to water; after standing for 15 to 50 days and cooling to 0° C. for several days the supernatant liquid was then analyzed both potentiometrically and nephelometrically for silver and chloride. By performing preliminary analyses the supernatant liquid was adjusted more closely to the end-point. In 1940, Baxter and Harrington[9] prepared potassium chloride via the chlorate and perchlorate; several crystallizations were carried out at each stage, and by comparison with silver they obtained K = 39·098.

Refs. p. 1557

Another determination of the KBr:Ag ratio made in the following year by McAlpine and Bird[10] – who prepared samples of potassium bromide by decomposition of the bromate and by causing potassium oxalate to react with pure bromine – gave K = 39•096.

From density and *X*-ray data, values of[11] 39•130 and[12] 39•091 have been calculated for the atomic weight of potassium. The isotope masses of ^{39}K and[13] ^{41}K when taken in conjunction with values of the ^{39}K/^{41}K abundance ratio (see page 1555) between 13•5 and 13•9 lead to atomic weights between 39•104 and 39•100.[14] Similar values result when other packing fraction data are combined with the abundance ratio.[15]

The fluctuations over the years in the atomic weight determinations of various workers are reflected in the internationally accepted value. From 1934 to 1951, and for many years prior to 1929, the International Atomic Weight of potassium was 39•096. Between 1929 and 1933 it was 39•10. The step-up resulted from Hönigschmid and Goubeau's[1-3] value of 39•104, and the reversion followed the report of several lower values.[6,7] In 1951 the accepted value again became 39•100.

Potassium extracted from the stems of potatoes fertilized with potassium chloride has been reported to have a higher atomic weight and to be more radioactive than ordinary potassium.[16] In other studies, however, no enrichment of the heavier isotope was found in either potato tops or roots.[17] An increased radioactivity – which, it was assumed, corresponded to a higher atomic weight – has been reported for potassium isolated as the cobaltinitrite from various human and other animal organs.[18] Normal atomic weights have been found for potassium extracted from the ash of cotton-seed hairs and wheat flour,[19] sugar-beet leaves and roots,[17,20] peas,[21] hard wood,[7] hop flowers,[8] and sunflower-seed hulls.[22]

The abundance ratio measurements of Brewer[23] (see page 1555) indicated some enrichment of ^{41}K in mature potato vines but not in young shoots; the effect was, however, much smaller than would correspond to the increased atomic weight referred to above.

Natural potassium consists of three isotopes – two stable isotopes ^{39}K and ^{41}K and the radioactive isotope ^{40}K. The two stable isotopes amount to 99•99% of the whole. A number of other potassium isotopes of short half-life have been produced artificially in nuclear reactions. A recent review,[24] which also summarizes methods of production and disintegration schemes, lists the following artificial isotopes: (see also page 2450).

Isotope	Half-life
^{37}K	1•2 sec.
^{38}K	7•6 min.
^{42}K	12•4 hr.
^{43}K	22•4 hr.
^{44}K	18 min.

Since the discovery by Aston[25] in 1921 of the two potassium isotopes with mass numbers 39 and 41, numerous determinations of their abundance ratio have been made. These are listed in Table XXIII, and with one exception (Manley[39]), they have all been obtained with the aid of the mass spectrograph. Manley's value was based on magnetic moment separation of the isotopes when a molecular beam of potassium is passed through a weak inhomogeneous magnetic field.

Bainbridge and Nier[44] in their 1951 review of abundance ratio data chose 13•48 ± 0•07 as the best value for the ^{39}K/^{41}K ratio. No isotope effect of free evaporation similar to that found with lithium (see page 66) occurs in the ion source of the mass spectrograph for potassium.[32,34] The existence of the

TABLE XXIII. - NATURAL $^{39}K/^{41}K$ ABUNDANCE RATIOS

Date	Authors	$^{39}K/^{41}K$ Ratio	Reference
1922–3	Dempster	18	26, 27
1934	Brewer and Kueck	13•88 ± 0•4	28
1935	Nier	13•96 ± 0•1	29
1935	Bondy *et al.*	16•2 ± 2•2	30
1935–9	Brewer	Mostly 14•20–14•25 but certain sources gave values between 12•6 and 14•6	23, 31–38
1936	Manley	13•4 ± 0•5	39
1936	Bondy and Vanicek	14•1 ± 0•1	40
1943	Cook	14•12 ± 0•28	41
1944	Paul and Pahl	13•96 ± 0•1	42
1948	White and Cameron	13•66 ± 0•1	43
1950	Nier	13•48 ± 0•07	44

potassium isotopes is also evident from the spectra of potassium compounds.[45]

Brewer has measured the $^{39}K/^{41}K$ ratio in a large number of animal, vegetable and mineral sources. These have included animal tissues and bones;[36] ocean and mineral waters;[33,35] rocks and soils;[38] and marine and land plants.[23] While in most sources the ratio was fairly constant between 14•20 and 14•25, there were a number of specific cases where the ratio deviated appreciably from its normal value: the abnormal values ranged from about 12•6 to 14•6. High ^{41}K contents were, for example, found in kelp, agar, bone marrow and in mineral formations (and their associated waters) believed to be of marine plant origin. High ^{39}K contents were observed in certain animal tissues. Other extensive measurements by Cook[41] on a variety of kelps, fossils and rocks of different geological ages have not, however, shown the same effect. The abundance ratio for all these sources was found to be constant within the experimental error of ±1%. Ingerson[45a] has reviewed work on the isotopic composition of potassium from various sources.

The question of which isotope of potassium is responsible for its natural radioactivity has received considerable attention. Until the mid-1930s it was believed that ^{41}K was responsible, but more recent work has demonstrated that ^{40}K – present at a concentration of about 0•01% – is the seat of the radioactivity.

Hevesy[46,47] in 1927 effected a partial separation of the potassium isotopes using a distillation process, and the measured increase[1,3] in the atomic weight of the residue corresponded to a 4•8% increase in the proportion of ^{41}K. At the same time the β-activity of the residue increased by 4•2%, and it seemed reasonable to ascribe the radioactivity of potassium to the isotope of mass 41. This conclusion was supported by several other workers,[48-51] and when in 1931 the subject was re-investigated by Hevesy and co-workers[52] to decide whether the radioactivity could be ascribed to a then hypothetical isotope, ^{40}K, the conclusion reached was again that active ^{41}K gave the best fit with the experimental results and that the existence of ^{40}K was unlikely. Opinion as to whether or not calcium was the product of the disintegration was at this time divided.[50-54] Aston[54] found no appreciable quantity of ^{41}Ca in very old minerals rich in potassium, indicating that the reactions $^{41}K \rightarrow {}^{41}Ca + \beta$ does not occur. Various other schemes suggested by Gamow[55] for the source of activity and decay of potassium were shown not to occur when tested experimentally.[56,57]

In 1935 suggestions were made that various features concerning the radioactivity of potassium could best be correlated by assuming the existence of a rare isotope ^{40}K.[57,58] In the same year, Nier[29,59] presented the first mass spectrographic evidence for the existence of this isotope, the $^{39}K/^{40}K$ ratio being 8600 ± 10%. The existence of ^{40}K was soon confirmed, first by Brewer[31] who, using an entirely different type of ion source, obtained an abundance ratio $^{39}K/^{40}K = 8300 \pm 100$, and then again by Sampson and Bleakney.[60] More recent determinations have indicated the $^{39}K/^{40}K$ ratio to be rather less than the above values: Nier[43] obtained 0·0119% ± 0·0001 for the abundance of ^{40}K (corresponding to $^{39}K/^{40}K = 7800$) whilst Reutersward[60a] obtained $^{39}K/^{40}K = 7900 \pm 40$ (^{40}K abundance = 0·0118%). In an earlier investigation, Bainbridge[61] had concluded that if the isotopes ^{40}K, ^{42}K and ^{43}K existed, their abundances relative to ^{39}K were less than one part in 1500, 600 and 300 respectively. That ^{40}K is responsible for the natural radioactivity of potassium was conclusively demonstrated by Smythe and Hemmendinger[62] who separated the potassium isotopes in a mass spectrometer incorporating a Geiger counter. ^{40}K was shown to be responsible for both of the known β-ray bands. The half-life of ^{40}K is about $1·4 \times 10^9$ years.

Later measurements[6,63] of the atomic weight of normal potassium and of the heavy potassium prepared by Hevesy have shown that in heavy potassium the ^{41}K content is increased by 7·4% rather than the 4·8% that had been reported earlier. Also, abundance ratio measurements on normal potassium and Hevesy's heavy potassium have given a figure of about 9% for the increase in the ^{41}K content: by interpolation it has been shown that an increase of about 4% would be expected in the ^{40}K content.[42] These more recent measurements on Hevesy's heavy potassium when taken in conjunction with the increased radioactivity are consistent with ^{40}K being the source of the radioactivity.

Other early explanations of the radioactivity of potassium attributed it to the isotope[64] ^{43}K and to admixture with traces of element 87.[65]

Determinations of the ^{40}K content of potassium from various terrestrial and meteoric sources have shown no differences that could not be ascribed to experimental error[65a-d] (5 to 10%).

In his early measurements of isotopic masses, Aston[66] showed that the masses of ^{39}K and ^{41}K approximated to whole numbers. The following values of isotopic masses are all on the physical scale of atomic weights taking $^{16}O = 16·00000$. From nuclear transmutation data, values of 38·97518 and 40·9739 have been obtained for the masses of ^{39}K and ^{41}K respectively.[67] Mass spectrometer measurements[13] have given $^{39}K = 38·97606 \pm 0·00003$ and $^{41}K = 40·97490 \pm 0·00003$ taking as standards the mass spectrometric values $^{1}H = 1·008146 \pm 0·000003$ and $^{12}C = 12·003842 \pm 0·000004$. Assuming values for ^{1}H and ^{12}C obtained from nuclear reaction energies, ($^{1}H = 1·008142 \pm 0·000003$ and $^{12}C = 12·003804 \pm 0·000017$,[68] the above mass spectrometer measurements yield $^{39}K = 38·97593 \pm 0·00006$ and $^{41}K = 40·97476 \pm 0·00006$.

Practically complete separation of the potassium isotopes has been carried out on a small scale using the mass spectrometer. Smythe *et al.*[69] in 1934 developed a high intensity mass spectrometer with a magnetic lens capable of focusing onto a slit all the positive ions of a given mass from a comparatively large source. With a Kunsman catalyst ion source an ion current of 0·1 ma. was obtained for ^{39}K. This permitted collection of ^{39}K at the rate of 1 mg. in 7 hours. The same instrument was later used by Smythe and Hemmendinger[62] to collect ^{40}K in amounts sufficient to demonstrate that it is responsible for the natural radioactivity of potassium (see above). These workers also collected 20·4 mg. of ^{39}K during the longest run of one week.

Production-scale mass spectrographs, originally developed to enrich uranium-235, have been used for the enrichment of potassium isotopes.[70,71] Enrichment of ^{40}K to over 10% isotopic purity was achieved in this way starting from its natural abundance of only 0·012%.[70] Starting with a potassium chloride charge that had been pile irradiated to increase the ^{40}K content to about 0·025%, several milligrams of 22% ^{40}K were obtained.[70]

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SECTION XLV

THE CHEMICAL PROPERTIES OF POTASSIUM

By Mrs. F. DICKINSON

Sodium and potassium resemble each other closely in their chemical properties except that potassium is generally more reactive.

Whereas potassium superoxide, frequently though less properly referred to as potassium tetroxide, is the stable oxide at room temperature, sodium monoxide, formed at low temperatures, is converted to a higher oxide only by heating in oxygen at high temperatures. According to Gilbert[1] many reports of explosions from handling potassium can usually be attributed to the formation of potassium superoxide which is very reactive. Potassium, unlike sodium, forms an explosive carbonyl with carbon monoxide and detonates when brought into contact with liquid bromine. Of all the hydrides of the Group 1 metals, potassium hydride is the least stable. Again, unlike sodium which forms acetylides with carbon, potassium forms solid solutions, although quite recently a solid solution of sodium in carbon has also been found to exist.

With regard to the handling of potassium and safety precautions to be taken, the same procedure should be adopted as for sodium except under conditions where potassium is known to behave differently and is more reactive. The potassium ion is somewhat toxic.[2]

A comparison of the properties of sodium and potassium is given by Gilbert.[1]

The Liquid-Metals Handbook, which first appeared in 1950, has now appeared in revised editions (1952, 1954, 1955) which contain a considerable amount of information on the liquid alkali metals and sodium–potassium alloys from 1920 with numerous references to original papers.

The surface of potassium on exposure to air emits a bluish glow considered to be due to the action of water vapour since it does not occur with dry oxygen.[3] The bright lustre is lost sooner than with sodium metal and in five minutes the surface is covered with a white film of potassium bicarbonate.[4–7]

Liquid potassium is more reactive on exposure to air than liquid sodium and may form higher oxides which react explosively with sodium, potassium, sodium–potassium alloy and organic materials. When handling liquid potassium an inert gas should be used to blanket the surface wherever possible.[2,8]

The interaction of oxygen with clean evaporated films of potassium at 0°C. to −183°C. has been investigated by Trapnell;[9] chemisorption occurs and the normal rapid oxygen adsorption is followed by a further process, probably oxidation. Although the metal surface does not chemisorb hydrogen, an oxygenated surface slowly takes up hydrogen at room temperature.

Potassium amalgam is oxidised by dry air or oxygen at room temperature to potassium superoxide, part of the mercury being also oxidised. On treatment with water, oxygen is evolved and a dark-green powder of mercurous oxide mixed with mercury is obtained.[10] Ostertag and Chassain[11] have confirmed the observation of Rinck and Chassain[10] that sodium amalgam is not peroxidised by air, even at 60°C. and with a larger contact area, but that when 0·035–0·50 mole fraction of potassium is added to sodium and amalgamated, the potassium superoxide, which is readily formed on exposure to air, catalyses the formation of sodium peroxide; in this case the mercury does not appear to be oxidised. The reaction of liquid potassium amalgam with oxygen has also been investigated by Hohn *et al.*[12] who find that potassium, unlike sodium, gives a higher oxide than the peroxide.

Potassium amalgam containing about 0·0003% of potassium, when brought into intimate contact at 0°C. with water in which oxygen is continuously dissolved, yields an aqueous solution containing 27 g. of hydrogen peroxide and 150 g. of caustic potash per litre, a yield of about 60% based on the caustic potash formed.[13]

Kraus and Whyte[14] have studied the oxidation of potassium in liquid ammonia solution and find that on slow oxidation potassium hydroxide and potassium amide are first formed, followed by further oxidation of the amide to potassium nitrite and potassium hydroxide. Rapid oxidation yields first potassium peroxide, K_2O_2, which in turn yields potassium tetroxide, (superoxide); there is no evidence of the formation of dipotassium trioxide, K_2O_3. The superoxide is prepared by Kraus and Parmenter[15] by the action of excess of oxygen at −50°C. in liquid ammonia; it is a cream coloured solid and is decomposed by water to the hydrated monoxide, $K_2O,3H_2O$, and oxygen. The peroxide or dioxide, K_2O_2, light yellow in colour, is formed by passing oxygen into potassium in liquid ammonia until all the potassium is used up; with water the hydrate $K_2O_2,2H_2O$ is formed and is decomposed by excess of water giving the hydrated monoxide, $K_2O,3H_2O$ and oxygen. The chocolate brown trioxide, K_2O_3, is formed when the calculated amount of oxygen is added to potassium in liquid ammonia at −33°C. The hydrate, K_2O_3,H_2O is decomposed by excess of water to the monoxide, $K_2O,3H_2O$ and oxygen.

Investigations of the structure of potassium superoxide[16–19] show the formula to be KO_2, not K_2O_4; the crystal is composed of the ions, K^+ and O_2^-.

Dipotassium trioxide, K_2O_3, is considered to be a mixture of potassium peroxide and superoxide.[20]

The following heats of formation, expressed as kg.-cal. per g.-mole, have been taken from Liquid Metals Handbook[8] $2K(c) + 0{\cdot}5O_2(g) \rightarrow K_2O(c)$, $\Delta H_{298} = -86{\cdot}14$; $2K(c) + O_2(g) \rightarrow K_2O_2(c)$; $\Delta H_{298} = -118$; $2K(c) + 1{\cdot}5O_2(g) \rightarrow K_2O_3(c)$, $\Delta H_{298} = -125$; $K(c) + O_2(g) \rightarrow KO_2(c)$, $\Delta H_{298} = -67$. Gilles and Margrave[21] give ΔH_{298} for the superoxide, KO_2, as $-67{\cdot}6 \pm 0{\cdot}8$ kg.-cal. per g.-mole.

Brewer and Mastick[22] on the basis of theoretical calculations state that at 1000°K. all the gaseous alkali metal oxides, with the exception of lithium monoxide, are unstable and dissociate.

Potassium reacts violently with water.[23] The alkali metals dissolve in liquid ammonia and in alkylamines and fused amides to give intense blue solutions, and it has been argued that similarly coloured solutions would be obtained in water were it not that the metals react extremely readily with this solvent. Wolthorn and Fernelius[24] have shown that by placing potassium in a short length of 6 mm. glass tubing and holding it at the bottom of a beaker of water so that the reaction takes place in a confined space, blue coloured patches are formed at irregular intervals along the tube. Very small coloured regions are also obtained with methyl alcohol, but not with ethyl alcohol. Jortner and Stein[25] have demonstrated the production of colour by the reaction of freshly distilled potassium with water at −3°C. with a maximum light absorption of 900 mμ. The colour decays if oxygen is added or the solution is warmed, when hydrogen is evolved. A bluish solution is obtained at −40°C.

with methyl or ethyl alcohol and the colour decays on admission of oxygen, on warming or on the addition of water.

The heat of reaction of potassium with an infinite quantity of water at 25°C. has been determined by Ketchen and Wallace[26] by calorimetry and found to be −47,190 ± 80 g.-cal./g.-atom. The heat of formation of aqueous potassium hydroxide at 25°C., calculated from the experimental values of the heat of reaction of potassium with water, is found to be −115·21 kg.-cal.[27] For the following reaction: $K(c) + H_2O(l) \rightarrow KOH(c) + 0{\cdot}5H_2(g)$, $\Delta H_{298} = -33{\cdot}46$ kg.-cal. per g.-mole.[8] Messer, Fasolino and Thalmayer[28] give the heat of hydrolysis corrected to infinite dilution at 25°C. for the reaction: $K(c) + H_2O(l) \rightarrow KOH(a) + 0{\cdot}5H_2(g)$, as $\Delta H_{298} = -47{\cdot}05 \pm 0{\cdot}10$ kg.-cal. per g.-mole.

The separation of the isotopes of hydrogen by the chemical decomposition of water containing a known amount of deuterium in neutral, acidic and alkaline media has been investigated by several workers.[29-33] The hydrogen evolved by the action of certain metals is burned and the percentage of deuterium in the water formed determined by density measurements. The value of the isotopic separation factor α is calculated by the relation $\log n_1'/n_1'' = \alpha \log (n_2'/n_2'')$, where n_1 and n_2 are the numbers of ^{1}H and ^{2}H atoms respectively in the reacting solution. The values of α increase in the order of their single-electrode potentials and photoelectric potentials for calcium, magnesium, aluminium, manganese and zinc and then decrease for chromium, iron and cobalt. The values of α for potassium, sodium and lithium (which is the order of the single-electrode potential and photoelectric potential) are irregular, being 1·9, 2·8 and 1·5 respectively. It is suggested that the mechanism of the reaction with the alkali metals is that water molecules are attached to the surface of potassium, sodium or lithium, through the oxygen atom, and hydrogen is then eliminated from two bound molecules, *i.e.* reduction by these metals does not proceed by an electrochemical process.[31]

Potassium hydride is formed when hydrogen is allowed to react with the metal at 350°C.; the reaction occurs more readily in the presence of calcium metal.[34]

In connection with the preparation of "active" hydrogen Venkataramaiah[35] describes experiments in which potassium is first heated at 200°C. and saturated with hydrogen; on raising the temperature gas is liberated which after chilling with ice reacts with powdered sulphur, as shown by the blackening of lead acetate paper, in two hours. Potassium treated with dry hydrogen at 670°C. gives off a gas which when chilled by ice and passed over powdered sulphur, blackens lead acetate paper in thirty minutes. Trapnell[9] has investigated the action of hydrogen on clean evaporated films of potassium at 0° to −183°C.; under these conditions hydrogen is not chemisorbed.

Hydrogen is absorbed by potassium deposited on the cathode of a discharge tube when a discharge is being passed. Analysis shows that potassium hydride is formed. Similar absorption of hydrogen occurs when the gas is ionised by alpha rays from polonium.[36] The absorption of hydrogen in potassium vapour arcs has also been investigated by Rusk[37,38] at temperatures of 40° to 180°C. and initial pressure of hydrogen of about 1 mm. The pressure falls owing to the formation of potassium hydride and the reaction is the more rapid the higher is the temperature. It is considered that the reaction is brought about by the presence of "active" hydrogen, formed at not less than 16 V. If potassium ions combined with hydrogen molecules then absorption of hydrogen should occur at 4·3 V., the ionisation potential of potassium.

Mohler describes a very slight luminescence obtained when potassium is heated in "active" hydrogen at low pressures.

Potassium, heated to 250°C. and exposed for twelve hours to hydrogen, activated by passage through a powerful electric discharge, and at a gas pressure of about 0·1 mm., shows the first doublet of the principal series 7665–99 A. very faintly.[39] Chemiluminescence and quenching reactions of the alkali metals with hydrogen have been studied by Magee and Taikei.[40] The reaction at 200°C.: $K + 2H \rightarrow K^* + H_2$, where the asterisk denotes electronic excitation and the prime vibrational excitation, occurs to only a slight extent.

The heat of hydrolysis of potassium hydride: $KH(c) + H_2O \rightarrow KOH(a) + H_2(g)$, corrected to infinite dilution and 25°C., has been found to be −31·89 ± 0·12 kg.-cal. per g.-mole. The heat of formation of the hydride, calculated from the heats of reaction of the metal and the hydride with water, is −15·16 ± 0·16 kg.-cal. per g.-mole. For the reaction $K(c) + 0{\cdot}5H_2(g) \rightarrow KH(c)$, ΔH_{298} is given as −13·6 kg.-cal. per g.-mole.[8] The heat of formation of potassium hydride, calculated from measurements of its dissociation pressures, is 14·110 kg.-cal. per g.-mole.[42]

The dissociation pressures of potassium hydride determined by Hérold[42] are given in Table I.

TABLE I.- DISSOCIATION PRESSURES OF POTASSIUM HYDRIDE

Temperature °C.	Vapour Pressure (mm.)
415·5	528
382·5	193
347·5	56
331·5	29·6
306·5	10·9
289	4·9

The above results are represented by the equation $\log p_{\mathrm{mm.}} = -6175/T + 11{\cdot}69$ where T = temperature on the absolute scale.

The following compounds of mercury with potassium are referred to in the literature: HgK, Hg_2K, Hg_3K, Hg_4K, Hg_8K;[43] HgK being bronze coloured, m.p. 178°C., and Hg_4K and Hg_8K, having a characteristic crystalline form;[44] HgK, Hg_2K, Hg_3K, Hg_4K, Hg_9K, $Hg_{12}K$.[45] The melting points and formulæ of the potassium mercurides as described by Grube[46] and compiled by Biltz, Weibke and Eggers[47] are: HgK m.p. 178°C., Hg_2K m.p. 279°C. with decomposition, Hg_3K, m.p. 204°C., Hg_7K_2 m.p. 197°C. with decomposition, $Hg_{18}K_5$ m.p. 194°C., Hg_9K_2 m.p. 173°C. and Hg_9K m.p. 70°C. There appears to be some doubt as to the composition of the compound richest in mercury; in their compilation of thermochemical data, Kubaschewski and Catterall[45] refer to it as $Hg_{12}K$ but give also alternative data for the composition Hg_9K.

TABLE II.- HEATS OF FORMATION OF SOLID COMPOUNDS IN K–Hg SYSTEM

	N_k	ΔH_{298} g.-cal./g.-atom
$\frac{1}{13}$ $Hg_{12}K$	0·077	(−2500)
$\frac{1}{10}$ Hg_9K	0·1	−3300
$\frac{1}{5}$ Hg_4K	0·2	−4600
$\frac{1}{4}$ Hg_3K	0·25	−5200
$\frac{1}{3}$ Hg_2K	0·33	−6100
$\frac{1}{2}$ HgK	0·5	−5900

In Table II N_k is the atomic fraction of 1 g.-atom of alloy e.g. if $N_k = x$ then 1 g.-atom of alloy = K_xHg_{1-x}. The brackets signify uncertainty.

Mercury and potassium show complete miscibility in the liquid phase. For other information on the K–Hg system see pages 1600–1610.

The heats of formation and free energies of the reaction products of potassium with fluorine and chlorine expressed as kg.-cal. per g.-mole are as follows: $K(c) + 0{\cdot}5F_2(g) \rightarrow KF(c)$, $\Delta H_{298} = -134{\cdot}46$, $\Delta F_{298} = -127{\cdot}42$;

$K(c) + 0{\cdot}5Cl_2(g) \rightarrow KCl(c)$, $\Delta H_{298} = -104{\cdot}2$, $\Delta F_{298} = -97{\cdot}6$.[2]

Potassium detonates when brought into contact with liquid bromine.[2]

In their investigation of atomic reactions of the alkali metals by the method of "highly dilute flames" (at low pressures of the order of 10^{-3} mm. and at a temperature such that alkali metal atoms are present and luminescence occurs), Beutler and Josephy[48] have found that when potassium atoms react with chlorine in the presence of atomic mercury there is an intensity increase in the spectrum of mercury. Ootuka[49] has also studied the reaction occurring between potassium atoms and chlorine at low pressures; to make the luminescence visible about 7 mol.-% of sodium is added. The suggested mechanism is: $K + Cl_2 \rightarrow KCl + Cl$; $K_2 + Cl \rightarrow KCl^* + K$; and $KCl^* + Na \rightarrow Na^* + KCl$; ($NaK + Cl \rightarrow KCl + Na$ is a probable mechanism). The asterisk denotes an increase in energy level. The heat of dissociation of K_2 or NaK is 12·5 kg.-cal.

Krocsák and Schay[50] report that the light emission of the highly attenuated flames of potassium vapour with the halogens is made up of (*a*) the red resonance doublet of potassium, (*b*) the second violet resonance doublet and (*c*) a continuum which extends over almost all the visible spectrum. The reaction $K + X_2 \rightarrow KX + X$, (where X = Cl or Br), and to a much smaller extent the reaction $K_2 + X \rightarrow KX + K$, occur in the gas space producing the red resonance doublet. In the first reaction every collision results in reaction. The second violet resonance doublet is partly due to the second reaction involving potassium molecules, and partly due to double excitations. The continuum originates on the wall of the vessel and is due to the secondary reaction $K + X \rightarrow KX$.

Lyalikov and Terenin[51] observe a luminescence from 2000 to 9000 A. when the alkali metal atoms are allowed to react with iodine. The first lines of the principal series of all the alkali metals are visible and the second lines of potassium, but no others. Faint bands, apparently continuous, are also observed. The pressure at which the reactions are carried out is <15 mm. An examination of potassium and iodine flames of high dilution and at low pressures has been made by Roth[52] who finds that the flames of potassium atoms and iodine vapour behave like those of potassium and chlorine or bromine. From a more exact examination of the observed effect of increase of temperature of the reaction zone and decrease of light, which is connected with the dissociation of potassium molecules to atoms, the heat of dissociation of potassium is found to be 18·7 kg.-cal. The constants of the elementary processes have been determined from distribution curves; the variation of the specific light emission with temperature and potassium pressure has also been found.

Molten iodine monochloride reacts with potassium with explosive violence.[53] A 100% conversion of potassium to potassium bromide and potassium dibromoiodide is obtained when potassium, in the form of sticks, is treated dropwise with molten iodine bromide. The mixture reacts explosively.[54]

In an account of the anomalous valencies exhibited by many elements, including the alkali metals, Klemm refers to the halogen compounds of potassium, rubidium and caesium, and gives the following examples of compounds which he describes as manifestly fluorine active: KF_3, $K(KF_6)$, $K(IF_6)$, $RbSbF_6{,}6RbF_3$, $Rb(SbF_6)$, $Rb(RbF_6)$.[55]

A very violent explosive reaction occurs when a mixture of potassium and hydrogen iodide is subjected to shock by striking with a hammer. Under similar provocation, a strong explosion occurs with iodine monobromide and a weak one with iodine.[56]

Fehér and Berthold[57] have studied the potassium–sulphur system and shown that the di- and tetra- sulphides, K_2S_2 and K_2S_4, can be prepared by the reaction of potassium with sulphur in liquid ammonia.

The action of sulphur on potassium in boiling toluene yields mixtures corresponding to $K_2S_{4\cdot7}$. The tri- and penta- sulphides are prepared by adding the calculated amount of sulphur to a solution of the monosulphide in absolute alcohol. The hexasulphide, K_2S_6, is prepared by melting sulphur with the pentasulphide in vacuo. All the above mentioned polysulphides are definite compounds and *X*-ray diffraction patterns and densities for these compounds are given.

The following compounds of potassium with sulphur are shown in the phase diagram on page 1616: K_2S, K_2S_2, K_2S_3, K_2S_4, K_2S_5, K_2S_6.

Chemiluminescence is observed in the low pressure reaction of potassium atoms with sulphur vapour at and above 300°C. The spectra of the various potassium reactions are continuous.[58]

When potassium is added to selenium monochloride, the mixture explodes violently at ordinary temperatures forming selenium and potassium chloride, which is slightly soluble in selenium monochloride.[59]

Whereas pure liquid ammonia undergoes no photo-decomposition in short ultra-violet light, 2144–2550 A., in the presence of the alkali metals hydrogen is evolved and the corresponding amide is formed. The quantum efficiency increases with concentration of the metal and reaches a maximum at 2300 A.

In the absence of catalysts such as metallic oxides and hydroxides, the reaction between the alkali metals and liquid ammonia is very slow at ordinary temperatures. In the presence of catalysts, amides and hydrogen are formed.[60]

Juza[61] has shown that under comparable conditions the times of reaction to form amides and hydrogen are: caesium, 15 min.; rubidium, 30 min.; potassium, 60 min.; sodium and lithium, several days, *i.e.* the heavier the alkali metal the more readily it reacts with liquid ammonia.

A study has been made of heterogeneous catalysts in liquid ammonia solutions by Burgess *et al.*[62] Although solutions of the alkali metals are relatively stable in liquid ammonia, a slow reaction does in fact occur. Earlier workers have shown that the time of reaction between potassium and liquid ammonia is shortened by the addition of asbestos; platinum black and oxides of iron are particularly effective so that as much as one gram of potassium amide is formed in 15 min. Platinised platinum, rusted iron and nickel foil are also efficient, and of the powdered catalysts tested ferrous oxide is the best. Whereas sodium amide poisons the catalyst, potassium amide does not do so.

Watt, Barnett, and Vaska[63] point out that the statement that the reaction of alkali metals with liquid ammonia is catalysed by metal oxides and salts is misleading because the compounds are reduced to the metals and these are responsible for the observed catalytic action.

Some of the most active catalysts are those commonly used for materials of construction. In Table III the results described refer to potassium and liquid ammonia at its boiling point and the reaction rate is expressed as c.c. of hydrogen evolved per hr. per g. of potassium, per sq. mm. of catalyst area × 10^2.

At the higher concentrations of potassium, the reaction between potassium and ammonia is of zero order, but as the concentration of potassium is decreased the reaction approaches first order. The use of any of the metals or alloys, even those ranging from tantalum to aluminium, as constructional materials would result in the liberation of sufficient hydrogen to constitute a hazard.

Juza *et al.*[64] give the heat of formation of potassium amide from its elements as 27 kg.-cal. per g.-mole.

The alkali metal is liberated from its fused amide when treated with

TABLE III.- EFFECT OF ADDITIVES ON THE FORMATION OF AMIDE AND HYDROGEN IN THE K-NH_3 SYSTEM

Additive	Reaction Rate	Additive	Reaction Rate
Tantalum	0·27	Phosphor Bronze	2·5
Silver	0·28	Monel	2·5
Titanium	0·28	Brass	2·7
Aluminium Clad Al.	0·30	Stainless Steel 430	3·3
Platinum	0·32	Stainless Steel 309	3·3
Zirconium	0·46	Hastelloy F–3	4·0
Aluminium	0·57	Nickel	4·6
Gold	1·1	Stainless Steel Carpenter 20	5·1
Aluminium Alloy 3 SHI4	1·2	Cobalt Steel FC	6·1
Copper	1·8	Hastelloy B–16	6·3
Stainless Steel 302	2·0	Berylco 25	7·0
Stainless Steel 347	2·3	Tungsten Steel GK	8·0
		Vanadium Steel GN	8·3

magnesium in an ammonia atmosphere: $Mg + 2KNH_2 \rightleftharpoons Mg(NH_2)_2 + 2K$; the equilibrium point is far to the right. Subsequent reactions also occur: $Mg(NH_2)_2 + 2KNH_2 \rightarrow Mg(NHK)_2,2NH_3$; $2NH_3 + 2K \rightarrow 2KNH_2 + H_2$. Calcium and aluminium also liberate potassium from its amide. The compound formed with calcium is $CaNK,2NH_3$; with aluminium it is AlN,NH_3 + adsorbed KNH_2. Zinc forms the compound $Zn(NHK)_2,2NH_3$. Cerium, thorium and manganese are slightly attacked by fused potassium amide whereas mercury, copper, cadmium, thallium, titanium, zirconium, tantalum, chromium, nickel, platinum and iridium are not noticeably attacked.[65]

Potassium amalgam reduces sulphur dioxide, potassium dithionite $K_2S_2O_4$ being formed; on standing, a secondary reaction occurs producing sulphide.[12]

Cueilleron[56] has shown that a very violent explosive reaction occurs when a mixture of potassium and sulphur dichloride is struck with a hammer; a strong explosion similarly occurs with sulphur dibromide.

Potassium does not react with nitrogen, which may in fact be used as an inert gas for the safe handling of the metal. An early description is given by Bornemann[66] of an apparatus for the preparation and storage of the lustrous metal in sealed glass tubes. The metal is placed on a clean metal sieve (1 mm. mesh) above a constriction in a long glass tube 15 mm. – 20 mm. diameter. After the tube is sealed, oxygen and carbon dioxide react with the metal leaving, after some hours, only nitrogen above the metal which is then melted and runs through the sieve leaving the impurities behind.

The activities of evaporated metal films in gas chemisorption have been studied by Trapnell between 0°C. and −183°C. The alkali metals show no chemisorption of nitrogen.[9]

When an electric discharge is passed through nitrogen with potassium present as a deposit on the cathode, nitrogen is found to be absorbed. A similar absorption occurs when nitrogen is ionised in the presence of potassium by the action of alpha rays from polonium. Chemical analysis shows that the absorption of gas is due to the formation of potassium nitride.[36] According to Moldenhauer and Mottig,[67] nitrogen activated by an electric discharge reacts with potassium to form azides; the reaction product also contains a small amount of nitride which is apparently formed from the azide.

The transfer of energy between active nitrogen, produced by the thermal decomposition of silver azide AgN_3, and potassium excites ultra-violet fluorescence in potassium vapour.[68]

Potassium arsenide, K_3As, is formed when the elements are heated together at 800 °C.[69]

A strong explosive reaction occurs when a mixture of potassium and arsenic trichloride or triodide is subjected to shock by striking with a hammer and a very violent explosive reaction similarly occurs with phosphorus pentachloride and tribromide.[56]

Disodium nitrite, Na_2NO_2, is formed when sodium nitrite in liquid ammonia solution is treated very slowly with a liquid ammonia solution of potassium; the same substance is formed by cathodic reduction of sodium nitrite. The disodium salt is very reactive towards moisture, air and carbon dioxide and explosions occur easily. Whereas it may be heated moderately in vacuo when it is in the pure state, it decomposes violently at 100°–130°C.[70]

Nitric oxide reacts with cold liquid potassium amalgam to form the compound, KNO. The amalgam must be shaken vigorously to ensure reaction.[71]

When nitryl fluoride, NO_2F, is passed over potassium, heated to start a reaction, the potassium burns with a lilac flame and a yellow solid is deposited. The product reacts with water, shows strong oxidising properties and gives evidence of the presence of a peroxide. Qualitative tests and *X*-ray examination show that potassium fluoride and potassium superoxide, KO_2, are formed and there may also be some potassium peroxide, K_2O_2.[72]

Paracyanogen, which contains a conjugated double bond system and no free CN groups and is believed to have a planar structure of 4–, 6–, or 10–membered rings, reacts with potassium on fusion to give potassium cyanide.[73]

According to Fredenhagen and Cadenbach,[74] molten potassium reacts with graphite, soot or active charcoal to give compounds in which the ratio of potassium to carbon is as shown in the formulae: KC_{16}, KC_8, KC_4, the presence of the compounds being indicated by breaks or discontinuities in a pressure–composition curve. The heat of formation is given as about 1500 g.-cal. per g.-atom of carbon. More recently Quarterman and Primak[75] have redetermined the heat of reaction of high density Acheson graphite with excess of potassium at several temperatures in the range 66–95 °C. by a calorimetric method, and give a mean value of 81 ± 2 g.-cal./g. of graphite as against the value of 125 g.-cal./g. of carbon reported by Fredenhagen and Cadenbach. Heats of reaction of potassium with pitch-bonded natural graphite, pitch-bonded lampblack, pitch-bonded petroleum coke and natural Ceylon graphite are in the range 72–90 g.-cal./g. of carbon. The reaction of liquid potassium with graphite, soot or active charcoal is a vigorous one and is accompanied by disintegration of the charcoal.[74] Tammann and Sworykin[76] have measured the shortening of small sticks of pressed retort carbon when heated in potassium vapour for 1·5 min. with the results given in Table IV.

TABLE IV.- ACTION OF POTASSIUM VAPOUR ON RETORT CARBON

Temperature °C.	Shortening of Retort Carbon Sticks, cm.
400–500	0·5
520–575	1·2
575–675	1·9
675–740	2·5
740–825	3·0

An accumulation of carbon powder on the surface of the evaporating metal can ignite in contact with air with a violent explosion.

Fredenhagen and Suck[77] by means of an improved technique,[74] have studied the binding of alkali metals with carbon at 400°–450 °C. for graphite and 400 °C. for soot, and shown that although the adsorption characteristics of the two forms of carbon are different, they take up the same amount of potassium at the same temperature and pressure. With graphite, equilibrium is attained after 22hr., with soot only after 60hr. The colour of the potassium–graphite compound (Siemens graphite) is at first dark blue-black; after an increase in potassium content the colour changes to copper-red. When Ceylon graphite, a coarsely crystalline graphite, is used the colour is at first steel-blue with a distinct metallic sheen and then becomes bronze coloured when the potassium content is increased. This change in colour seems to occur suddenly after the large increase in potassium content. The compound K_2C_2, *i.e.* potassium acetylide, could not be detected in the graphite–potassium system. Diamond does not react with potassium.

Schleede and Wellmann[78] have investigated the structure of the potassium–graphite compounds by *X*-ray methods and find that the brown substance described by Fredenhagen *et al.*[74,77] has a layer lattice, potassium planes alternating with the basal planes of the graphite. When the metal planes are complete, the composition corresponds with the formula C_8K. When heated at a higher temperature, a black substance is formed in which every two graphite planes are followed by a potassium plane; the composition is then represented by the formula, $C_{16}K$.

After the distillation of potassium from the graphite–potassium system, the graphite has its original structure.

Hofmann and Frenzel[79] report that *X*-ray diffraction data for the stoicheiometric compound, C_8K, show no change in the distance between carbon atoms within the ring layers, while the distance between the layers is increased from 3·38 A. in graphite to 5·34 in C_8K. Treatment with mercury regenerates graphite.

Much later work on the action of potassium on graphite by Hérold,[80] who has prepared temperature–composition curves for the system graphite–potassium, describes the compounds KC_8, KC_{24}, and KC_{40}. A sudden change in composition near 107°C. is accompanied by a change in colour from brown ochre to deep blue.

By the slow formation and decomposition of graphite–potassium compounds, Rudorff and Schulze[81] have shown that a whole series of compounds of ideal formulae KC_8, KC_{24}, KC_{36}, KC_{48}, KC_{60} is formed, and spacings have been measured by *X*-ray analysis for compounds up to KC_{60}. All these compounds are weakly paramagnetic.

The effect of potassium on the mechanism of the activation of charcoal has been studied.[82] The adsorptive capacity of a potassium-containing charcoal, activated in a carbon dioxide atmosphere, decreases linearly with the potassium content. The adsorptive capacity of charcoal to which potassium carbonate is added is also decreased. It is suggested that the decreased activity is due to an excessive activation of the burning process which destroys the porous outer surface of the charcoal particles and hinders diffusion to the centre.

An explosive carbonyl is formed when potassium reacts with carbon monoxide.[2] The kinetics of the reaction have been investigated by Shushunov,[83] using special apparatus and procedures designed for studying such reactions.[84] Potassium is coated on a wire in an enclosure which is then evacuated to about 10^{-5} mm. Hg; an electric current is passed through the wire and any gases occluded in the alkali metal are drawn off. The metal is then slowly vapourised and some is collected on a suspended copper foil, the weight deposited being determined by the elongation of a fine spiral suspension, using a vertically moving microscope. Carbon monoxide is then admitted and the increase in weight determined. For the reaction $xK + xCO \rightarrow (COK)_x$ the increase in weight of potassium should be 72%; actually it is 78·5%. After pumping off excess carbon monoxide, water vapour is slowly added; the observed increase in weight is 27–31%, which gives a ratio of $H_2O/COK = 1$ approximately. It it suggested that the reaction between potassium carbonyl and water proceeds according to the equation: $(COK)_2 + 2H_2O \rightarrow CH_2OH.COOK + KOH$. Gases are given off in the reaction with water. The reaction of potassium carbonyl with oxygen gives inconclusive results because it is violent and part of the reaction product is lost by spattering.

Iodine pentoxide, used for the determination of carbon monoxide, must be free from potassium which may originate from the barium chlorate used in the preparation of the pentoxide. A high and constant reactivity of iodine pentoxide can be ensured by removing potassium from the barium chlorate by repeated recrystallisation.[85]

Metallic potassium, exposed to the action of a solution of aluminium chloride in phosgene, reacts immediately; a gas is evolved and the metal is slowly corroded. An insoluble compound which appears to be a phosgenate of a slightly soluble double salt of potassium chloride with aluminium chloride is formed.[86] Potassium and phosgene react explosively when subjected to shock.[56] (See Table V, page 1571).

At elevated temperatures potassium reduces carbon dioxide to carbon monoxide and carbon.[1] An explosive reaction occurs when solid carbon dioxide and potassium are subjected to shock.[1,56,87–89]

Dilute potassium amalgam reacts with carbon dioxide to yield potassium oxalate. The percentage yields at 20°, 100°, 200°, 225° and 250°C. are 25, 60, 72, 68 and 61% respectively. There appears to be a relation between yield and half-wave potential of the various amalgams used for the above reaction, page 440, Part 1 "Chemical Properties of Sodium". According to Henglein and Sontheimer[90] the dependence of the yield of oxalate on the potential of the amalgams is due to the fact that carbon dioxide is reduced not only to oxalate but also further to carbon monoxide: $2M + CO_2 \rightarrow M_2O + CO$, $M_2O + CO_2 \rightarrow M_2CO_3$. The smaller is the yield of oxalate the greater is the yield of carbonate. Hohn, Fitzer and Nedwed[91] have made a detailed examination of the reaction with sodium amalgam, and the results apply also to potassium amalgam. They show that the reaction velocity is practically independent of concentration; that the conversion rate is increased by stirring although the total yield is unchanged; that the reaction rate seems to increase with decreasing temperature and that the presence of impurities affects the reaction. Thus oxygen produces some peroxide, water vapour gives some carbonate and/or bicarbonate along with some carbon monoxide, and hydrogen and nitrogen do not affect the net result. No carbon monoxide is formed if moisture and air are rigidly excluded.

Schwabe and Gebhardt[92] have made thermodynamic calculations which show that whereas the amalgams of sodium, potassium, lithium, calcium, barium, manganese and zinc should react with carbon dioxide to form oxalates, only the amalgams of lithium, calcium, barium, manganese and zinc should also reduce carbon dioxide to carbon monoxide. Although detailed experiments have been carried out only with sodium amalgam, the results are probably applicable to potassium amalgam. The effect of motion of the amalgam on the rate of formation of oxalate is greater than Hohn *et al.* reported. The regeneration of the surface and not a diffusion process determines the rate, if the concentration (Na) is greater than 0·007%. The temperature and pressure effects of carbon dioxide on the rate of reaction are concentration effects; as the carbon dioxide pressure increases the rate increases linearly. The amount of oxalate formed decreases as air is added with carbon dioxide; with 50% of air no oxalate is formed. Earlier references to the reaction of amalgams with carbon dioxide are given.[93,94]

Potassium is used in the vapour form as a promoter in various gas reactions, such as ammonia synthesis at 450°C. and 200 atm. pressure in the presence of osmium or iron catalysts, or the production of hydrogen and higher hydrocarbons from methane at 1000°C. with a nickel catalyst.[95] Although the catalytic activity of potassium is extremely small compared with that of sodium, the sodium–potassium alloys, particularly NaK and NaK_2, are exceptionally active at the temperatures and pressures generally used for hydrogenation in the presence of nickel. In the laboratory, 1 kg. of the unsaturated compound C_8H_{10} can easily be converted to C_8H_{14} quantitatively in the presence of 2% of magnesium oxide and 10% of alloy in a hydrogenizer in three hours.[96]

The reactions of potassium with metals are described on pages 1597–1618.

The reaction of potassium with the oxides of molybdenum and tungsten are described by Hérold and Hatterer.[97] The action of potassium vapour on tungsten oxide, WO_3, yields the potassium salt, K_2WO_3, which is in equilibrium with the composition $K_{1.5}WO_3$ between 140° and 170°C. Compositions in the range K_2WO_3–$K_{1.5}WO_3$ are changed by the action of water to $3K_2WO_4$ + W. The reactions are accompanied by the production of hydrogen and caustic potash. Potassium vapour and the oxide of molybdenum, MoO_2, yield the compound $K_{1.16}MoO_2$ which is reversibly transformed at sufficiently high temperatures to $K_{0.66}MoO_2$. Potassium vapour and the potassium salt, K_2MoO_4, produce $K_{2.66}MoO_4$. Compositions in the range $K_{1.16}MoO_2$–$K_{2.66}MoO_2$ yield $5K_2MoO_4$ + 3MoO by the action of water; those in the range $K_{1.5}MoO_3$ – K_2MoO_3 produce K_2MoO_4 + 2MoO. The composition, $K_{2.66}MoO_4$, gives $8K_2MoO_4$ + Mo. Each of these reactions is accompanied by the production of hydrogen and caustic potash, except the last which yields only caustic potash, Hérold and Hatterer[98] have shown that by the controlled action of potassium vapour on molybdic anhydride, MoO_3, the compounds, K_2MoO_3 and $K_2Mo_2O_6$ are formed. The reaction: $2K_2MoO_3 \rightleftharpoons K_3Mo_2O_6 + K$ is reversible.

Potassium vapour produced by heating calcium carbide and potassium chloride at 600–700°C. at 1 mm. Hg pressure reacts with a number of metal compounds to give the free metal which is distilled off and condensed as a powder. Any residual potassium or its compounds may be removed from the product by washing first with methanol and then with water. In some cases the metal is redistilled. Antimony has been prepared in this way from its compounds Sb_2O_3, Sb_2S_3, Sb_2OS_2, bismuth from its oxide, Bi_2O_3, beryllium from its fluoride or chloride, magnesium from a mixture of potassium and magnesium chlorides, zinc and calcium from their oxides, sulphides and silicates, calcium and lead from their oxides, sulphides and chlorides, chromium, molybdenum, tungsten, uranium from their sulphides, from mixtures of potassium chloride and the corresponding chlorides, from alkali or alkaline earth chromates, molybdates, tungstates or uranates. Uranium has also been obtained from the halides, Na_2UCl_6 and Na_2UF_6. Yields are of the order of 90% and the purity of the metal is generally 99·5%. Alloys may also be obtained by the reduction of mixtures.[99]

Equilibria in the molten state between potassium and sodium and their hydroxides, chlorides, bromides, iodides and fluorides have already been described in the section on the Chemical Properties of Sodium. (see Part 1, page 440).

Titanium and zirconium are produced by the exothermic reaction between their gaseous halides and molten potassium. External heat is required to start the reaction at 750°–900°C. which will then continue if continuous feeding of the halide, the rate of supply of the reducing metal and the area of the container are correlated to maintain the reaction temperature. Air is expelled from the apparatus by the vapour of the halide which is held at above 1 atm.[100] Many of the references given for the reduction of titanium tetrachloride by sodium refer also to reduction by alkali metals in general including potassium.

Köhler[101] describes a process by means of which titanium tetrachloride is reduced by potassium amalgam to titanium amalgam; the mixture of amalgam and metal chloride is separated from excess mercury by distilling under reduced pressure and the residue is extracted for titanium. The process is carried out in a closed cycle; potassium chloride solution is electrolysed in a chlorine–alkali electrolytic cell against a flowing mercury cathode and the potassium amalgam formed is passed into the reaction vessel.

Glasser and Hampel[102] have patented a process for the recovery of titanium, zirconium, hafnium, thorium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten and uranium in a pure crystalline form by the reduction of a halide of the metal, preferably a chloride, with an alkali amalgam such as potassium or sodium. The metals are not appreciably soluble in mercury or in the alkali metal salt produced in the reaction and do not form stable compounds with mercury. Many of the references already given for the reduction of metal halides to metals by means of sodium amalgam refer to amalgams of the alkali metals which would include potassium amalgam.

A continuous process for the production of titanium from titanium tetrachloride and a mixture of liquid potassium and lithium amalgams of composition K:Li 4:1 by weight, is described by Hohn.[103]

Pure zirconium may be obtained in the same way from solid zirconium tetrachloride.

The mechanism of the reaction of potassium atoms with mercuric chloride has been studied by several workers.[104-108] The results have been reviewed by Bawn.[109] The primary reaction is $K + HgCl_2 \rightarrow KCl + HgCl$; the secondary reaction: $K + HgCl \rightarrow KCl^* + Hg$; $KCl^* + K \rightarrow K' + KCl \rightarrow K + h\nu$. The luminescence, which accompanies the reaction, is weaker than in the case of the halogens and is found to be due to the secondary reaction. The reaction between potassium vapour and cupric chloride or bromide vapour at 300 °C. causes the emission of light having the same spectrum as the corresponding cuprous halides. The reaction is thought to be a wall reaction as in the case of mercuric chloride. Potassium vapour reacts with solid cupric halide giving solid potassium chloride and gaseous cuprous halide. The surface light is intense whereas the gas space light is weak. The colour of the surface light from the cupric chloride reaction is bluish green extending from 5500–3900 A., almost completely in the region of the cuprous chloride spectrum: the colour of the surface light from the cupric bromide reaction is blue or bluish violet and the spectrum extends from 5000–3800 A., corresponding to the cuprous bromide spectrum.

The spectrum for the space light is the same for both salts.[105,109]

According to Polanyi and Schay, when potassium vapour at 0·01 mm. pressure is brought into contact with the vapour of tin tetrachloride, tetrabromide or tetraiodide reaction occurs with the emission of an intense and continuous luminescence; reduction to the dihalide occurs and there is no deposit on the walls of the apparatus. Tin tetrachloride gives a visible blue light, the tetrabromide a green and the tetraiodide a yellow light. With tin tetrachloride, no hydrogen chloride can be detected when hydrogen is admitted to the system. The luminescence reaction is thought to be due to the combination of two $SnCl_3$ radicals formed by the action of potassium vapour on the tetrachloride: $K + SnCl_4 \rightarrow KCl + SnCl_3$; $SnCl_3 + SnCl_3 \rightarrow SnCl_2 + SnCl_4 + h\nu$.[109,110] Ogg and Polanyi[111] consider that the luminescence produced is due to the diabatic process: $K + SnCl_4 \rightarrow KCl + SnCl_3$; $2SnCl_3 \rightarrow SnCl_2$

+ $SnCl_4$ + *hν*.

A violent reaction occurs between vanadium oxychloride and potassium at 100°C.[112]

Mixtures of certain halides with potassium react explosively when subjected to shock by striking with a hammer as shown by the results obtained by Cueilleron,[56] given in Table V.

TABLE V.- EFFECT OF MECHANICAL SHOCK ON MIXTURES OF METALLIC POTASSIUM WITH VARIOUS HALIDES

Halide	Type of Explosion	Halide	Type of Explosion	Halide	Type of Explosion
NH_4Br	Weak	AgI	Weak	HgI_2	Strong
NH_4I	Weak	ZnF_2	Weak	HgCl	Strong
SrI_2	Weak	$ZnCl_2$	Strong	BBr_3	Very violent
$CuCl_2$	Strong	$ZnBr_2$	Strong	AlF_3	Strong
$CuBr_2$	Strong	ZnI_2	Strong	$AlCl_3$	Strong
CuCl	Strong	CdF_2	Weak	$AlBr_2$	Strong
CuBr	Strong	$CdCl_2$	Strong	ThCl	Weak
CuI	Strong	$CdBr_2$	Strong	ThBr	Strong
$CuCl_2$,2KCl	Weak	CdI_2	Strong	CCl_4	Very violent
$CuCl_2$,$2NH_4Cl$,$2H_2O$	Strong	HgF_2	Strong	$SiCl_4$	Strong
AgF	Strong	$HgCl_2$	Strong	$SnCl_2$	Strong
AgCl	Weak	$HgBr_2$	Strong	$SnCl_4$	Strong
SnI_4 + S	Strong	$CoCl_2$	Very violent	BaF_2	None
PCl_5	Very violent	$CaBr_2$	Very violent	$BaCl_2$	None
PBr_3	Very violent	NiF_2	Weak	$BaBr_2$	None
$AsCl_3$	Strong	$NiCl_2$	Strong	UCl_4,2KCl	None
AsI_3	Strong	$NiBr_2$	Strong	MnF_2	None
$SbCl_3$	Strong	NiI_2	Strong		
$SbBr_3$	Strong	LiCl	None		
SbI_3	Strong	LiBr	None		
$BiCl_3$	Strong	LiI	None		
$BiBr_3$	Strong	NaF	None		
BiI_3	Strong	NaCl	None		
VCl_5	Strong	NaBr	None		
SCl_2	Very violent	NaI	None		
SBr_2	Strong	NH_4Cl	None		
CrF_3	Weak	MgF_2	None		
$CrCl_4$	Strong	$MgCl_2$	None		
$MnCl_2$	Strong	$MgBr_2$	None		
$MnBr_2$	Weak	CaF_2	None		
MnI_2	Weak	$CaCl_2$	None		
$FeCl_3$	Very violent	$CaBr_2$	None		
$FeBr_3$	Very violent	CaI_2	None		
$FeCl_2$	Strong	SrF_2	None		
$FeBr_2$	Very violent	$SrCl_2$	None		
FeI_2	Very violent	$SrBr_2$	None		

Explosions have also been obtained with potassium and the oxychlorides of copper, lead and vanadium, the iodates of sodium and silver, the peroxide and sulphate of lead, and boric acid. Such reduction of oxygen-containing compounds is no doubt very general.

When monochlorosilane, SiH_3Cl, is brought into contact with potassium by means of a vacuum process which excludes air, moisture and fat, the surface of the potassium becomes blue and further action is prevented by the film thus formed. After heating for several hours up to 300°C., a deep seated reaction takes place, resulting in the formation of silicon, potassium hydride, potassium chloride and hydrogen.[113]

Potassium may be used in place of sodium in the reaction with hydrogen and boron to prepare boron hydride.[114,115]

Hydrogen is evolved when potassium is dissolved in molten aluminium chloride monoammine: $AlCl_3,NH_3 + 3K = AlCl_3,K_3N + 1{\cdot}5H_2$.[116]

The reaction of alkali metal vapours on porcelain has been examined by Tammann and Sworykin[76] and the results given in Table VI refer to the temperature and time required to destroy the bottom of a porcelain crucible, 2 mm. thick.

TABLE VI.- ACTION OF ALKALI METAL VAPOURS ON PORCELAIN

Lithium	Sodium	Potassium
at 465°C. after 7·5 min.	at 740°C. after 24 min.	at 740°C. after 40 min. thickness is 0·03 mm.

Thus lithium vapour reacts more quickly and potassium vapour more slowly than sodium vapour.

MacDonald and Stanworth[117] describe a glass especially resistant to potassium and lithium usable for the preparation of alkali metals. The glass is of the type used in sodium discharge tubes with an inner lining of a borate glass which is free from silica. Other references to the action of alkali metals on glasses or ceramics are given under Sodium (see Part 1, page 499).

Corrosion of materials by liquid metals is discussed by Miller[2] and many references to the literature are given. The evaluation of materials according to their corrodibility is summarised in Table VII; ratings are based principally on data established for static tests and are as follows: "good" = rate of attack <1 mils/year, "limited" = >1, <10; "poor" = >10. The results are based chiefly on a limited number of relatively small-scale laboratory tests and their principal value is that they can serve to eliminate many materials from consideration, and to guide the selection of more promising materials; they do not warrant the final selection of a material.

TABLE VII.- RESISTANCE OF MATERIALS TO LIQUID POTASSIUM AT 300°, 600° AND 800°C.

Materials	Temp. °C.	Rating
Pure iron	800	Good
Pure iron	600	Good
Pure iron	300	Good
Mild carbon steel	800	Poor
Mild carbon steel	600	Limited
Mild carbon steel	300	Good
Low chromium steel with V, Mo or Si	800	Not tested
Low chromium steel with V, Mo or Si	600	Limited
Low chromium steel with V, Mo or Si	300	Good
2–9% chromium steel with Ti, Mo or Si	800	Limited
2–9% chromium steel with Ti, Mo or Si	600	Good
2–9% chromium steel with Ti, Mo or Si	300	Good
Ferritic stainless steels 12–27% Cr	800	Good
Ferritic stainless steels 12–27% Cr	600	Good
Ferritic stainless steels 12–27% Cr	300	Good

continued on following page

TABLE VII.- CONTINUED

Materials	Temp. °C.	Rating
Austenitic stainless steels 18–8 and 25–20 Cr–Ni	800	Good
	600	Good
	300	Good
Grey cast iron	800	Poor
Grey cast iron	600	Poor
Grey cast iron	300	Limited
Aluminium	800	Not tested
Aluminium	600	Poor
Aluminium	300	Poor
Beryllium	800	Limited
Beryllium	600	Good
Beryllium	300	Good
Chromium	800	Good
Chromium	600	Good
Chromium	300	Good
Copper base alloys with Al, Si or Be	800	Poor
Copper base alloys with Al, Si or Be	600	Good
Copper base alloys with Al, Si or Be	300	Good
Copper base alloys with Zn or Sn	800	Not tested
Copper base alloys with Zn or Sn	600	Poor
Copper base alloys with Zn or Sn	300	Not tested
Cobalt-base alloys	800	Good
Cobalt-base alloys	600	Good
Cobalt-base alloys	300	Good
Molybdenum, Columbium, Tantalum, Tungsten	800	Good
Molybdenum, Columbium, Tantalum, Tungsten	600	Good
Molybdenum, Columbium, Tantalum, Tungsten	300	Good
Nickel and nickel alloys with Fe, Cr, Mo	800	Good
Nickel and nickel alloys with Fe, Cr, Mo	600	Good
Nickel and nickel alloys with Fe, Cr, Mo	300	Good
Nickel alloys with copper	800	Limited
Nickel alloys with copper	600	Good
Nickel alloys with copper	300	Good
Platinum, Gold and Silver	800	Poor
Platinum, Gold and Silver	600	Poor
Platinum, Gold and Silver	300	Not tested
Titanium	800	Limited
Titanium	600	Good
Titanium	300	Good
Zirconium	800	Not tested
Zirconium	600	Good
Zirconium	300	Good
Alumina	800	Limited
Alumina	600	Good
Alumina	300	Good
Graphite (dense)	800	Poor
(Ordinary graphite is rapidly and completely	600	Good
dispersed resulting in a mushy slurry)	300	Good
Beryllia (dense)	800	Good
Beryllia (dense)	600	Good
Beryllia (dense)	300	Good

continued on following page

TABLE VII.- CONTINUED

Materials	Temp. °C.	Rating
Magnesia (crucible)	800	Poor
Magnesia (crucible)	600	Limited
Magnesia (crucible)	300	Not tested
Porcelain and other Silicates	800	Not tested
(see ref. 76)	600	Not tested
	300	Good
Pyrex glass	800	Not tested
Pyrex glass	600	Poor
Pyrex glass	300	Limited
Titania and Zirconia	800	Not tested
Titania and Zirconia	600	Not tested
Titania and Zirconia	300	Not tested
Fused Quartz	800	Not tested
Fused Quartz	600	Not tested
Fused Quartz	300	Good

The above results also apply to liquid sodium and sodium-potassium alloy except for graphite (dense) at 800°C. An investigation of the corroding effect of liquid potassium on magnesium, silver, aluminium, tungsten, chromium, copper, iron, cobalt and nickel has been made by Eldred.[118]

Potassium reacts with oxygen-containing salts, nitrates, sulphates, hydroxides, chromates, manganates, silicates, but not with the carbonate or monoxide of potassium or with molten baths of potassium halides, amide and cyanide or hydride.[1]

Alkali metal dispersions including potassium dispersions, which are stable against settling and agglomeration and in which the dispersed metal does not exceed 50μ in size, are obtained by preparing an emulsion of the metal in an inert hydrocarbon in the presence of an emulsifying agent, as is illustrated by examples given for sodium (see Part 1, page 501).

Metal vapours may be separated from gases by absorption in molten tin distributed as discrete drops throughout a mass of granular refractory. The absorptive bed is particularly useful for removing metals with boiling points of 500°–1000°C., e.g. sodium, potassium, arsenic, mercury, cadmium, or zinc.[120] An example involving the separation of sodium vapour and carbon monoxide is given in Part 1.

For other references to the chemistry and industrial uses of the alkali metals, and to the handling, hazards and precautions necessary when working with the metals, see Part 1, page 440, The Chemical Properties of Sodium.

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REACTIONS OF POTASSIUM IN LIQUID AMMONIA

A. Inorganic Reactions

Reactions of inorganic substances with solutions of metals (including the alkali metals) in liquid ammonia have been described by Watt[1] and numerous references to original papers up to January 1st, 1949, are given.

In the absence of catalysts, the rate of interaction of metals with liquid ammonia is negligible compared with the rates of most of the reactions studied in these solutions.

An earlier review of the reactions of solutions of metals in liquid ammonia, with numerous references, is also given by Fernelius and Watt.[2]

There is no conclusive evidence that the rare gases or the transitional or rare earth elements react with liquid ammonia solutions of metals.

The reduction products have not always been isolated, but their compositions have for the most part been determined. In many cases the compositions of the reaction products have been established by means of potentiometric titrations, points of inflexion indicating compound formation.

By the slow oxidation of potassium in liquid ammonia, potassium monoxide is first formed but is then ammonolysed to give potassium hydroxide and amide. The amide is subsequently further oxidised to potassium hydroxide and nitrite: $K_2 + 0{\cdot}5O_2 \rightarrow K_2O$; $K_2O + NH_3 \rightarrow KOH + KNH_2$; $2KNH_2 + 1{\cdot}5\,O_2 \rightarrow KOH + KNO_2$.

When the oxidation of potassium is carried out at a rapid rate, the initial product is potassium dioxide which on further oxidation is converted to potassium superoxide, KO_2, referred to by the authors as potassium tetroxide, K_2O_4. The reactions are: $K_2 + O_2 \rightarrow K_2O_2$; $K_2O_2 + O_2 \rightarrow K_2O_4\,(2KO_2)$. To isolate the dioxide, the reaction is interrupted as soon as the free metal has disappeared. The dioxide is a white compound sometimes tinged with yellow owing to the presence of some potassium superoxide. It does not react with liquid ammonia even on long standing but is readily oxidised to the superoxide. The dioxide is very reactive; on admitting air, or water, considerable heat is developed and explosions may occur. After an explosion in air or water the products of reaction are coloured red, yellow and purple. The superoxide, KO_2, is a stable compound unaffected by dry air. It dissociates at temperatures above 300°C. The process is reversible but the dissociation pressures appear to depend on the oxygen content of the solid phase. The final product of dissociation has a composition corresponding to the formula, K_2O_3. This compound has not been detected in liquid ammonia solutions of potassium treated with oxygen. On exposure to moist air potassium superoxide loses oxygen irreversibly between 100° and 200°C.[3]

Kraus and Parmenter[4] describe potassium superoxide as a cream coloured solid formed by adding excess of oxygen to a liquid ammonia solution of potassium. Decomposition of the oxide with water gives $K_2O,3H_2O + \frac{1}{2}O_2$. The dioxide is described here as light yellow in colour; it forms a hydrate with water, $K_2O_2,2H_2O$ and with excess of water yields $K_2O,3H_2O + \frac{1}{2}O_2$. The trioxide, K_2O_3, formed from the calculated amounts of oxygen and potassium in liquid ammonia at −33 °C., is chocolate brown in colour and is first hydrated with water to K_2O_3,H_2O and then decomposed by excess of water to the monoxide hydrate $K_2O,3H_2O$ and oxygen.

Potassium superoxide in liquid ammonia reacts with stoicheiometric amounts of zinc nitrate and copper nitrate tetra-ammoniate but not with lithium and calcium nitrates. Solid superoxides cannot however be isolated because they are too unstable. The reactions with zinc nitrate are: $Zn(NO_3)_2 + 2KO_2 \rightarrow Zn(O_2)_2 + 2KNO_3$; $Zn(O_2)_2 \rightarrow ZnO_2 + O_2$. This is a method by which anhydrous peroxides may be obtained. Some decomposition of the peroxide to the monoxide results in ammonolysis, hydroxide and amide being formed. This occurs to a larger extent with copper nitrate tetra-ammoniate because the copper ion catalyses decomposition of the peroxide to monoxide which then gives rise to copper hydroxide and copper amide.[5]

Potassium superoxide is less soluble in liquid ammonia than is sodium superoxide.[6] Other references to the action of oxygen on potassium in liquid ammonia are given.[1,7,8]

The reaction of ozone with potassium in liquid ammonia at −70°C. has been studied.[9] A gelatinous white precipitate of potassium hydroxide is first formed, the blue colour of the metal solution disappears, the precipitate then dissolves and a deep-orange solution and a precipitate form. Much nitrate is present in the reaction product. About 2/3 to 3/4at. of oxygen is present per mol. of hydroxide. Potassium ozonide is probably formed but the compound is too unstable to permit isolation and examination. The readiness of formation and the stability of ozonides of the alkali metals increase in the order: sodium, potassium, rubidium, cæsium.

Sulphur reacts very rapidly with potassium in liquid ammonia at −33°C. giving first a white, apparently amorphous precipitate of potassium monosulphide. Further reaction with sulphur yields a light yellow or orange disulphide which in turn is converted to the tetrasulphide; this compound is soluble in liquid ammonia giving an orange yellow solution. Further quantities of sulphur are at first readily dissolved and the higher polysulphide formed produces a red coloured solution. The reactions are represented by the equations: $2K + S \rightarrow K_2S$; $K_2S + S \rightarrow K_2S_2$;, $K_2S_2 + 2S \rightarrow K_2S_4$; $K_2S_4 + (x-4)S \rightarrow K_2S_x$.[10]

Potassium monosulphide, which is white when pure and may be kept unchanged in pure nitrogen or under vacuum, becomes coloured on exposure to moist air. Zintl and co-workers[11] have investigated the crystal structure of this compound by *X*-ray methods and find that the side of the lattice, *a*, is 7·391 A. and the calculated density 1·80; the experimental value for the density is 1·74. Klemm, Sodomann and Langmesser[12] give $a = 7{\cdot}39$A. and the calculated density as 1·809, in good agreement with the above results. The disulphide is yellow, the trisulphide brown, the tetrasulphide wine-red and the pentasulphide dark brown. The trisulphide exhibits pyroelectricity.

Watt and Otto[13] describe an apparatus for use in potentiometric titrations of liquid ammonia solutions of potassium with solutions of potassium polysulphides in the same solvent at −38°C., giving complete procedure and operational details. The polysulphides are prepared *in situ* and potentiometric titrations carried out in the presence of either sodium or potassium iodide. The results are given in Table VIII.

TABLE VIII.- POTENTIOMETRIC TITRATIONS OF POTASSIUM POLYSULPHIDES WITH POTASSIUM IN LIQUID AMMONIA AT −38°C.

Composition of Polysulphide	Normality	Iodide Added	Compounds Indicated at Points of Inflexion
K_2S_{11}	0·0516	111·1 mg. KI	K_2S_4, K_2S_2, K_2S
K_2S_8	0·0443	100·5 mg. NaI	K_2S_4, M_6S_4

where M = K and/or Na

When sodium iodide is present in place of potassium iodide, there is no end point corresponding to the monosulphide; moreover a different compound of formula M_6S_4 is found. This difference in behaviour could be attributed to the altered solubility relationships due to the presence of sodium ion.

Selenium reacts very readily with potassium in liquid ammonia at −33°C. Initially a white, sparingly soluble and apparently amorphous precipitate of potassium monoselenide is formed. This reacts with more selenium to form soluble potassium diselenide which in turn forms very soluble polyselenides. The average composition of the higher polyselenides in equilibrium with selenium is $K_2Se_{5\cdot0}$; it is probable that this composition represents a mixture of tetraselenide and hexaselenide. The reactions are: $2K + Se \rightarrow K_2Se$; $K_2Se + Se \rightarrow K_2Se_2$; $K_2Se_2 + Se \rightarrow K_2Se_3$; $K_2Se_3 + Se \rightarrow K_2Se_4$; $K_2Se_4 + (x - 4)Se \rightarrow K_2Se_x$, where $x = 5–6$. Very dilute solutions of the selenides are: colourless K_2Se; pale red K_2Se_2; pale yellowish green K_2Se_3; pale yellow K_2Se_4, pale yellow K_2Se_5.[10] The crystal structure of the monoselenide has been investigated by Zintl *et al.*;[11] the lattice constant $a = 7{\cdot}676$ A., the calculated density is 2·29. Klemm, Sodomann and Langmesser[12] have prepared potassium monoselenide from its elements in liquid ammonia and examined its crystal structure. The lattice side is 7·67 A., and the calculated density 1·809. The above authors have also investigated the system K_2Se–Se by thermal and *X*-ray analyses. The following compounds are found: K_2Se, K_2Se_2, K_2Se_3, K_2Se_4 and K_2Se_5. There is no evidence of the existence of a hexaselenide. The triselenide, K_2Se_3, exhibits strong pyroelectricity.

Potassium monotelluride, K_2Te, has been prepared from its elements in liquid ammonia. It is white and insoluble in liquid ammonia. Its crystal structure has been examined by *X*-ray methods and the side of the lattice found to be 8·152 A., giving a calculated density 2·51 as against the experimental value 2·52.[11] Klemm, Sodomann and Langmesser have also prepared the monotelluride in this way and report the lattice dimension as 8·14 A.[12]

Reactions of phosphorus and potassium in liquid ammonia have been investigated by Brauer and Zintl[14] and by Evers.[15] Incomplete reaction occurs with red phosphorus,[14] but by using white phosphorus the compound K_3P_2 is obtained. This compound is even less soluble than the corresponding lithium and sodium compounds and the colour at the end point is a deeper orange than with lithium and sodium, a red polyphosphide being formed. The compound K_3P_2 may be reduced with lithium or sodium in liquid ammonia to a compound of empirical formula M_2P. It is unlikely that these compounds are mixtures since on removal of the solvent they appear to be uniform. The probability of the formation of a dimer, $K_3P_2–P_2K_3$ is discussed. Normal phosphides have not been detected.

Arsine reacts vigorously with potassium in liquid ammonia at −78°C., the colour of the solution changing from the intense blue of the alkali metal solution to green and finally to a brilliant yellow. Hydrogen is liberated. The reaction is: $K + AsH_3 \rightarrow KAsH_2 + \frac{1}{2}H_2$. On removing the solvent ammonia a pale yellow, almost white solid is left. It does not take up ammonia of crystallisation, nor is it ammonolysed. It may be kept unchanged for 60 hr. in a vacuum at room temperature. There is no evidence of decomposition below 115°C. but at this temperature it begins to darken, becomes brown and liberates hydrogen. Decomposition is complete at 175°C. and the residue, which is a polyarsenide of potassium, is blue-black. Potassium dihydrogen arsenide reacts vigorously with air liberating much heat, and the brown solid formed presumably contains arsenic and solid arsenic–hydrogen compounds. A liquid ammonia solution of potassium dihydrogen arsenide when treated with ammonium bromide gives off arsine: $KAsH_2 + NH_4Br \rightarrow KBr + NH_3 + AsH_3$. The compound $KAsH_2$ and ammonia are formed when arsine is passed into a liquid ammonia solution of potassium at −78°C. to which a few milligrams of ferric nitrate have been added to catalyse the formation of potassium amide: $KNH_2 + AsH_3 \rightarrow KAsH_2 + NH_3$. Methyl chloride reacts with potassium dihydrogen arsenide in liquid ammonia at −78°C. to form methylarsine and potassium chloride: $KAsH_2 + CH_3Cl \rightarrow KCl + CH_3AsH_2$. On treatment with potassium in liquid ammonia at −78°C., methylarsine is converted into the potassium derivative: $CH_3AsH_2 + K \rightarrow CH_3AsHK + \frac{1}{2}H_2$. Addition of ammonium bromide regenerates methylarsine:

$CH_3AsHK + NH_4Br \rightarrow KBr + CH_3AsH_2 + NH_3$.[16]

Potentiometric titrations of liquid ammonia solutions of bismuth tri-iodide with a solution of potassium in liquid ammonia give points of inflexion corresponding to the compositions K_3Bi_3, K_3Bi_5 and Bi.[17]

Liquid ammonia solutions of bismuth oxyiodide, BiOI, are reduced at room temperature by potassium: $BiOI + 3K + NH_3 \rightarrow Bi + KI + KOH + KNH_2$; the reaction with potassium amide is represented by the equation: $BiOI + KNH_2 \rightarrow BiONH_2 + KI$. Excess of alkali metal forms bismuthides, but less readily in the case of potassium than with sodium.[18]

Potentiometric titrations of thallium chloride $TlCl_3$ with potassium in liquid ammonia have been carried out by Watt and co-workers.[19] Elemental thallium produced competes in the reduction of the chloride; there is evidence that the products of the reaction are KTl and elemental thallium.[19]

Silver iodide and chloride are reduced by excess of potassium in liquid ammonia to silver, and hydrogen is evolved. The precipitated silver catalyses the reduction of the halides; it is not reactive towards air. Silver cyanide is also reduced to silver with evolution of hydrogen; some hydrogen is adsorbed on the silver precipitate which is sometimes pyrophoric. The corresponding reaction occurs with silver cyanate; silver is precipitated but the ion OCN^- is not reduced. With silver thiocyanate silver is precipitated and there is some reduction to the ion CN^-. Silver precipitated from liquid ammonia solutions of potassium with silver iodide or cyanide catalyses the reaction of calcium with ammonia.[20]

Zintl, Goubeau and Dullenkopf,[21] by means of potentiometric titrations of liquid ammonia solutions of potassium with lead iodide solutions in liquid ammonia, have found evidence, illustrated in Table IX, for the presence of the compound K_4Pb_9.

TABLE IX.- POTENTIOMETRIC TITRATIONS OF LEAD IODIDE WITH POTASSIUM IN LIQUID AMMONIA

Temperature	In Reaction Vessel	In Burette	Point of Inflexion	Composition at Point of Inflexion
−50°C.	12·27 mg. K in 75 ml. NH_3	91·1 mg. PbI_2 in 76·18 ml. NH_3	49·57 60·84	$K_4Pb_{8\cdot80}$ Pb
−50°C.	about 0·1 g. K in 75 ml. NH_3	about 0·7 g. PbI_2 in 71·98 ml. NH_3	49·96 61·26	$K_4Pb_{8\cdot85}$ Pb

In spite of working with very dilute solutions no compound analogous to Na_4Pb_7 can be detected. A green solution of the compound K_4Pb_9,xNH_3 in liquid ammonia is described by Zintl and Kaiser.[22]

Ferrous bromide, $FeBr_2$, when treated with potassium in liquid ammonia at −33·5°C. yields an insoluble mixture containing iron, the nitride, Fe_3N, and one or more products from the reaction of potassium amide and ferrous bromide. The iron produced in this reaction is pyrophoric, does not contain adsorbed hydrogen, and is inactive as a catalyst for the hydrogenation of certain olefines at 30°C. and hydrogen pressure of 2 atm.[23] In a later paper Watt[17] reports that the reduction of ferrous bromide with potassium in liquid ammonia is very complex and apparently does not involve the formation of the ion Fe^+.

Nickel salts such as the chloride, bromide, iodide, thiocyanate, acetate and cyanide are reduced by potassium in liquid ammonia at −33·5°C., nickel being precipitated. Small amounts of nickel amide are also formed when the nickel salt is present in excess. The free nickel formed is pyrophoric, probably because of adsorbed hydrogen, and is an excellent catalyst for the reaction between sodium, potassium or calcium and ammonia: $NiBr_2 + 2K \rightarrow Ni + 2KBr$; $2K + 2NH_3 \rightarrow 2KNH_2 + H_2$; $NiBr_2 + 2KNH_2 + 2NH_3 \rightarrow 2KBr + Ni(NH_2)_2,2NH_3$. The last reaction may be minimised by a short time of reaction and by the rapid addition of the alkali metal in an amount only slightly in excess of the stoicheiometric amount. Nickel having a purity of 98–99% may be obtained by adding an ammonium salt to convert the amide to a soluble nickel salt: $Ni(NH_2)_2,2NH_3 + 2NH_4I \rightarrow NiI_2,6NH_3$. The catalytic activity of the nickel produced is considered to be due to the presence of adsorbed hydrogen. Adsorption is partially or completely inhibited by the presence of iodide ion during the reduction process. Nickel prepared from nickel iodide is not appreciably pyrophoric and is a very poor hydrogenation catalyst. The catalytic activity of nickel produced from nickel bromide is very much reduced if the reaction is carried out in the presence of potassium iodide.[1,24-26] The relative catalytic activities of nickel produced by the reduction of nickelous bromide with liquid ammonia solutions of different alkali metals have been examined by Watt and Mayfield. The rates of solution of the alkali metals in liquid ammonia and the rates of the reaction with nickelous bromide increase from lithium to cæsium. The solubilities of the bromides and the amides increase in the same direction. The nickel obtained with the different alkali metals differs only in surface area, the catalytic activity per unit area being substantially constant for all the reducing metals, *i.e.* lithium, sodium, potassium, rubidium and cæsium.[27]

Nickel amide, $Ni(NH_2)_2$, is reduced to nickel in liquid ammonia solutions of potassium.[24] In the reduction of nickel acetate to nickel the acetate ion is not reduced.[24]

Magnesium catalyses the formation of potassium amide in liquid ammonia: $K + NH_3 \rightarrow KNH_2 + \frac{1}{2}H_2$; magnesium reacts with the amide: $Mg + 2KNH_2 \rightarrow Mg(NH_2)_2 + 2K$; more potassium amide is formed which reacts with magnesium amide to give the sparingly soluble, crystalline potassium ammonomagnesiate, $Mg(NHK)_2,2NH_3$.[28,29]

Potentiometric titrations of the iodides of gallium-III and indium-III with potassium in liquid ammonia give evidence for a three electron change resulting in the formation of the elemental metal.[19]

Potassium reacts with aluminium in liquid ammonia as follows: $Al + 3KNH_2 \rightleftharpoons Al(NH_2)_3 + 3K$; $Al(NH_2)_3 + KNH_2 \rightarrow Al(NH_2)_2NHK.NH$; $3K + 3NH_3 \rightleftharpoons 3KNH_2 + 1{\cdot}5H_2$.[28]

The possible reaction mechanisms for the system Al iodide–K–KNH_2–liquid ammonia have been discussed by Watt and co-workers[19] on the basis of the results of potentiometric titrations. The reaction with potassium amide produces aluminium amide, $Al(NH_2)_3$, which is converted to the potassium derivative, $KAl(NH_2)_4$, by reaction with potassium amide.[19]

Liquid ammonia solutions of potassium react rapidly and exothermally with aluminium triiodide at −70°C. with evolution of hydrogen, until an apparent end point is reached (*i.e.* temporary retention of the blue colour of the metal solution). The reaction then proceeds at slow rates similar to those of the alkali metals with ammonia. The solid products isolated are mixtures of ammonobasic compounds, $Al(NH_2)_2I$ and $Al(NH_2)_3$. There is no evidence of the presence of the ions Al^{++} or Al^{+}.[30]

Potassium in liquid ammonia solution reacts with ammonium nitrate to form ammonia, potassium hydroxide and dipotassium nitrite according to the equation: $NH_4NO_3 + 3K \rightarrow NH_3 + KOH + K_2NO_2$.[20]

Ammonium azide, NH_4N_3, reacts vigorously with potassium in liquid ammonia to give potassium azide, ammonia and hydrogen: $K + NH_4N_3 \rightarrow KN_3 + NH_3 + \frac{1}{2}H_2$.[31]

The heat of reaction of dilute solutions of ammonium bromide and chloride in liquid ammonia with potassium in the same solvent has been measured in a liquid ammonia calorimeter at −33°C. From the known heat of solution of potassium in pure liquid ammonia the heat of reaction of the dilute metal solution with ammonium ion has been calculated. A mean value of 40·4 kg.-cal. is obtained for all the alkali metals examined, *i.e.* for lithium, sodium, potassium and caesium. It is considered by Coulter and Maybury[32] that the reactions which occur are: $M + NH_4^+ \rightarrow M^+ + NH_3 + \frac{1}{2}H_2$ followed by $e^-{}_{am} + NH_4^+{}_{am} = NH_3(g) + \frac{1}{2}H_2$ (gas).

The hydrogen liberated in the above reaction has been used *in situ* to reduce many organic compounds. The presence of an excess of ammonium bromide in a solution of potassium in liquid ammonia at −33·5°C. does not, however, affect the reaction which takes place with silver-I iodide, bismuth-III oxide or germanium-IV oxide in the absence of ammonium bromide.[1]

Ammonium chromate and dichromate are partially reduced by potassium in liquid ammonia and give a green solution; some potassium amide is also formed.[1]

Potassium nitrate is reduced by potassium in liquid ammonia;[17,20] the nitrate ion is reduced to nitrite and dipotassium nitrite, or potassium hydronitrite, K_2NO_2, is precipitated according to the equations: $KNO_3 + 2K + NH_3 \rightarrow KNO_2 + KNH_2 + KOH$; $KNO_2 + K \rightarrow K_2NO_2$. This compound, unlike the corresponding sodium salt, is not explosive.

Sodium nitrite is converted to potassium sodium hydronitrite, $KNaNO_2$, by the action of potassium in liquid ammonia solution.[33]

Silver nitrate is reduced to silver.[20]

The reduction of cobalt nitrate by potassium in liquid ammonia has been investigated by Watt and Otto[13] and later by Watt, Choppin and Hall.[17] The mechanisms of the reactions first suggested are:

(*a*) $Co(NO_3)_2 + 2K \rightarrow Co(NO_2)NO_3 + K_2O$
(*b*) $K_2O + NH_3 \rightarrow KOH + KNH_2$
(*c*) $Co(NO_2)(NO_3) + KNH_2 \rightarrow Co(NO_2)(NH_2) + KNO_3$
(*d*) $Co(NO_2)(NH_2) + KOH + NH_3 \rightarrow Co(NH_2)_2 + KNO_2 + H_2O$
(*e*) $KNO_3 + 2K \rightarrow KNO_2 + K_2O$

or alternatively:

(*f*) $Co(NO_3)_2 + 4K \rightarrow Co(NO_2)_2 + 2K_2O$
(*g*) $2K_2O + 2NH_3 \rightarrow 2KOH + 2KNH_2$
(*h*) $Co(NO_2)_2 + 2KNH_2 \rightarrow Co(NH_2)_2 + 2KNO_2$

Watt and co-workers[17] later preferred the first group, (*a*) to (*e*).

Potassium permanganate is reduced by potassium in liquid ammonia to potassium manganate, K_2MnO_4, and manganese oxides; this reaction occurs rapidly and is followed by a much slower reaction: $K_2MnO_4 + 4K + 3NH_3 \rightarrow MnO + 3KNH_2 + 3KOH$. Potassium permanganate is reduced by potassium amide in liquid ammonia forming potassium manganate, ammonia and nitrogen: $6KMnO_4 + 6KNH_2 \rightarrow 6K_2MnO_4 + 4NH_3 + N_2$.[1]

Cobalt oxide, Co_2O_3, is reduced to CoO and finally to cobalt when treated with liquid ammonia solutions of potassium at 0°C. The extent of the reaction depends upon the ratio of the reactants Co_2O_3/K used. Both oxides react slowly with liquid ammonia solutions of potassium amide at room temperature to form complex mixtures.[34]

Ferric oxide, Fe_2O_3, catalyses the conversion of potassium in liquid ammonia to potassium amide; this reacts with the oxide to form ferrous oxide, FeO, and iron.[35] Ferrous oxide is reduced only to a limited extent by potassium in liquid ammonia at 0°C.[34]

Nickel oxide, Ni_3O_4, also catalyses the conversion of potassium to the amide in liquid ammonia but to a less extent than does ferric oxide. An intractable mixture of insoluble products is obtained when the nickel oxide is treated with potassium in liquid ammonia at 25°C. The oxide, NiO, also catalyses the formation of potassium amide but to a lesser extent than does the higher oxide, Ni_3O_4. At 0°C. the oxide, NiO, is reduced by potassium in liquid ammonia to nickel; the reduction is 0·3, 0·5, 1·4 and 4·3% respectively when 2, 4, 8 and 12 equivalents of potassium are used. The oxide does not react with potassium amide in liquid ammonia in 72hr. at 100°C.[35]

The addition of ammonium chloride and hydrogen sulphide to the reaction product of potassium and carbon monoxide in liquid ammonia (in the absence of air and moisture) produces a mixture of three organic acids, one of which has been identified as glycollic acid.[36]

The imide, Sn(NH), reacts with potassium in liquid ammonia to form a compound, K_4Sn_x.[37] Compounds such as K_4Sn_x are salt-like, *i.e.* electrolytes, both in structure and in behaviour. The metallicity of the compounds is considered to be a molecular rather than an atomic property.[38]

According to Burgess and Eastes[24] potassium tetracyanonickelate, $K_2Ni(CN)_4$, treated with potassium in liquid ammonia at −33·5°C., gives a bright red precipitate of potassium tricyanonickelate, $K_2Ni(CN)_3$. They were however unable to reduce this compound to the zero oxidation state of nickel, *i.e.* $K_4Ni(CN)_4$, by addition of excess of potassium. Burbage and Fernelius[39] carrying out the reaction at 0°C. were able to reduce potassium tetracyanonickelate, $K_2Ni(CN)_4$, from its II oxidation state to the I state, $K_2Ni(CN)_3$, and the zero state, $K_4Ni(CN)_4$ but were only sometimes successful in obtaining the zero state of oxidation at −33·5°C. By potentiometric titrations Watt and co-workers[40] have shown that by working at or near −33·5°C. two one-electron steps are involved: $[Ni(CN)_4]^{=} - e^{-} \rightarrow [Ni(CN)_4]^{-}$, followed by $[Ni(CN)_4]^{-} - e^{-} \rightarrow [Ni(CN)_4]^{0}$ which is slow at −33·5°C.; and that with excess of potassium one two-electron step is involved, the compound $K_2Ni(CN)_4$ being converted directly to $K_4Ni(CN)_4$ without passing through the intermediate stage of $K_2Ni(CN)_3$. The compound $K_4Ni(CN)_4$, when freed from the solvent, is a copper-coloured solid which on treatment with water gives a red solution and liberates hydrogen.[41]

Potassium hexacyanocobaltate, $K_3Co(CN)_6$, is first reduced by potassium in liquid ammonia to potassium tetracyanocobaltate: $K_3Co(CN)_6 + 2K^+ + 2e^- \rightarrow 2KCN + K_3Co(CN)_4$, and then to potassium tetracyanocobaltate, $K_4Co(CN)_4$.[40]

Potassium tetracyanopalladate, $K_2Pd(CN)_4$, is reduced by potassium in liquid ammonia to potassium tetracyanopalladate, $K_4Pd(CN)_4$, which is obtained as a light yellow crystalline precipitate. On treatment with water it yields hydrogen, hydrogen cyanide, and metallic palladium.[39,41]

Potassium hexacyanochromate (III) is reduced by potassium in liquid ammonia to a dark brown product extremely susceptible to oxidation by air and moisture.[41]

A yellow product, sparingly soluble in liquid ammonia and possessing strong reducing properties, is obtained when potassium hexacyanomanganate (III) is reduced by potassium in liquid ammonia. The reaction might be represented thus: $2K_3Mn(CN)_6 + 5K \rightarrow K_5Mn(CN)_6 + K_6Mn(CN)_6$. The empirical formula of the reaction product is $K_{11}Mn_2(CN)_{12},2NH_3$ and it contains unipositive and zeropositive manganese, atom for atom.[41]

Potentiometric titrations of ammines of rhodium, iridium, and platinum with solutions of potassium and potassium amide in liquid ammonia have been made by Watt and co-workers.[42] With tetrammine platinous bromide, $[Pt(NH_3)_4]Br_2$, and potassium in liquid ammonia at −38°C. the initial clear solution becomes progressively darker until near the end of the titration when the colour fades rapidly and a pale yellow precipitate forms. Excess of potassium added at this stage fails to produce the characteristic blue colour of the alkali metals in liquid ammonia or the anticipated potential for a liquid ammonia solution of potassium amide. The reduction proceeds to an ammine of platinum of zero state of oxidation, *i.e.* it is exactly a 2-electron change and the +1 oxidation state of platinum is not encountered. One g.-mole of the bromide requires exactly 2 g.-atoms of potassium. *trans*-Diammine platinous bromide gives identical results.

Similar reduction of bromopentammine iridium (III) bromide, $[Ir(NH_3)Br]Br_2$, results in a rapid discharge of the blue colour of the original solution and the slow formation of a cream coloured precipitate. The reaction is complex and observed changes in potential do not correspond to any reasonable or probable reactions. Titration of the same bromide with potassium amide in liquid ammonia solutions in the presence of an iron wire catalyst produces a finely divided white precipitate and the colour changes are from colourless to yellow, orange, and then bronze. Evidence is obtained in this case for stepwise replacement of bromide by amide groups followed by conversion of the resultant iridium (III) amide to, probably, a potassium amidoiridate (III). The reactions may be represented thus: $IrBr_3 + KNH_2 \rightarrow Ir(NH_2)Br_2 + KBr$; $Ir(NH_2)Br_2 + KNH_2 \rightarrow Ir(NH_2)Br + KBr$; $Ir(NH_2)_2Br + KNH_2 \rightarrow Ir(NH_2)_3 + KBr$; $Ir(NH_2)_3 + 3KNH_2 \rightarrow K_3Ir(NH_2)_6$ or $Ir(NH_2)_3 + 3KNH_2 \rightarrow Ir(NHK)_3 + 3NH_3$.

Bromopentammine rhodium (III) bromide and potassium amide in liquid ammonia react similarly but only so far as to yield rhodium (III) amide.[42]

Potassium reacts with tributylboron in liquid ammonia according to the equation: $Bu_3BNH_3 + K \rightarrow Bu_3BNH_2K + \frac{1}{2}H_2$. The reaction carried out in ethylamine in place of ammonia does not yield stoicheoimetric amounts of hydrogen; unstable reaction products are obtained with trimethylboron.[43]

The diammoniate of diborane, $B_2H_6,2NH_3$, reacts with potassium in liquid ammonia according to the equation: $K + B_2H_6,2NH_3 \rightarrow KBH_4 + BH_2NH_2 + \frac{1}{2}H_2 + NH_3$:, potassium borohydride and aminoborine are obtained on removing the solvent. Some ammonolysis occurs on evaporation of the solvent: $BH_2NH_2 + xNH_3 \rightarrow BH_{2-x}(NH_2)_{1+x} + xH_2$, but to a much smaller extent with potassium as reducing agent than with sodium and lithium.[44]

Boron trifluoride ammine, BF_3,NH_3, reacts with potassium in liquid ammonia to give hydrogen, potassium fluoride and the amido compound BF_2,NH_2. The reaction may be expressed by: $K + BF_3,NH_3 \rightarrow \frac{1}{2}H_2 + KF + BF_2NH_2$.[45]

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B. Organic Reactions in Liquid Ammonia

An account is given by Watt[1] of organic reactions with solutions of metals, including potassium, in liquid ammonia. General mechanisms are described with references to original papers up to January 1949.

Many of the reactions already described for solutions of lithium and sodium apply also to potassium solutions.

Saturated hydrocarbons are not attacked; benzene does not react at low temperatures,[2] nor does toluene.[3] When water is added to a mixture of toluene and potassium in liquid ammonia, less than the theoretical amount of hydrogen is evolved and a highly unsaturated liquid product, boiling range 110°–115°C., is obtained. Wooster and Mitchell[4] have found that neither potassium nor potassium amide reacts with toluene, tetraphenylmethane, phenylethane or dibenzyl in liquid ammonia; they do however react with diphenylmethane, triphenylmethane, 1:2:2-triphenylethane and 1:1:2:2-tetraphenylethane to give intense red or orange-yellow potassium salts; only a slight reaction occurs with methyltriphenylmethane and 1:2:2:2-tetraphenylethane and potassium in liquid ammonia; potassium amide does not react. The carbon–carbon bond in the compound $CPh_3.CPh_3$, *i.e.* hexaphenylethane, is ruptured by potassium in liquid ammonia and the free radical reacts further to form potassium triphenylmethide.[1,4,5]

The alkali metal salts of hydrocarbons react readily with alkyl and aryl halides and are used in syntheses.

Stilbene reacts with potassium in liquid ammonia forming a reddish-brown solution of the dipotassium salt, PhCHK.CHK.Ph, which is stable at −78°C., and stable enough at −33·5°C. for its colour to be apparent, but which ammono-

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lyses immediately at room temperature forming dibenzyl: $PhCH{=}CHPh + 2K \rightarrow PhCHK.CHK.Ph$; $PhCHK.CHKPh + 2NH_3 \rightarrow PhCH_2.CH_2Ph + 2KNH_2$.

Triphenylethylene and potassium in liquid ammonia yield a product which on treatment with methyl sulphate is converted to 1:2:2-triphenylpropane, $Ph_2C(CH_3).CH_2Ph$.

Tetraphenylallene, $Ph_2C{=}C{=}CPh_2$ reacts with potassium in liquid ammonia to give probably a mono-potassium derivative, $Ph_2CKCH_2CHPh_2$ or possibly a di-potassium compound. Crystalline methyl, ethyl and benzyl derivatives obtained from the alkali metal compound are identical with those prepared from tetraphenylpropylene.

In the reduction of phenylated olefines with the alkali metals in liquid ammonia solution, the phenyl groups are not attacked, but the double bonds in the side chain may be saturated and the corresponding phenylated paraffin obtained by decomposing the organo-alkali compound with ammonium chloride.[6]

When 1:1-diphenylpropylene is added slowly to a concentrated solution of potassium in liquid ammonia, so that the alkali metal is always present in excess, a potassium derivative is formed from which 1:1-diphenylpropane may be obtained by treatment with ammonium chloride followed by removal of ammonia, washing and drying and distillation under reduced pressure. The potassium derivative reacts with benzyl chloride to give a saturated hydrocarbon: $Ph_2C{=}CHCH_3 + 2K \rightarrow Ph_2CK.CHK.CH_3$; $Ph_2CK.CHKCH_3 + NH_3 \rightarrow Ph_2CK.CH_2CH_3 + KNH_2$; $Ph_2CKCH_2CH_3 + PhCH_2Cl \rightarrow KCl + Ph_2C(Et).CH_2Ph$. If the potassium is present in only slight excess, subsequent treatment with benzyl chloride yields 1:1:4-triphenylbutylene: $Ph_2C{=}CHCH_3 + K \rightarrow Ph_2C{=}CHCH_2K + H$; $Ph_2C{=}CHCH_2K + PhCH_2Cl \rightarrow KCl + Ph_2C{=}CH.CH_2CH_2Ph$.

A reaction between phenylated paraffins and potassium amide in liquid ammonia occurs only when the benzohydryl group, Ph_2CH-, is present.[7]

The polymerisation of styrene in liquid ammonia is catalysed by potassium.[8]

Potassium acetylide is formed by adding a liquid ammonia solution of the metal to acetylene in liquid ammonia at such a rate that there is no excess potassium present. In this way reduction of some of the acetylene to ethylene is minimised.[9] Numerous references are given by Watt[1] to the use of alkali metal acetylides or alkali metal substituted acetylides in the synthesis of organic compounds.

Naphthalene is reduced by potassium in liquid ammonia, a 1:2:3:4-tetrapotassium addition product being first formed and about 75% ammonolysed even at −33·5°C. The suggested mechanism of the reaction is: $C_{10}H_8 + 4K \rightarrow C_{10}H_8K_4$; $C_{10}H_8K_4 + 4NH_3 \rightarrow C_{10}H_{12} + 4KNH_2$. Slow ammonolysis of excess potassium in liquid ammonia also occurs as shown by evolution of hydrogen during the reaction: $K + NH_3 \rightarrow KNH_2 + \frac{1}{2}H_2$.[10]

Usually halogens are removed quantitatively from organic compounds by solutions of metals in liquid ammonia: the reaction may be used for the quantitative determination of halogens in organic compounds.

Triphenylchloromethane with potassium in liquid ammonia yields the mono-potassium derivative Ph_3CK.

Condensation products of allyl or substituted allyl halides are prepared by treatment with alkali metals in liquid ammonia solution.[1]

Alcohols react readily with alkali metals in liquid ammonia solution forming alkoxides and hydrogen. Potassium alkoxides are generally more soluble than the sodium compounds: $ROH + K \rightarrow ROK + \frac{1}{2}H_2$, where R is CH_3-, C_2H_5-, $n\text{-}C_4H_9-$, $iso\text{-}C_4H_9-$, $iso\text{-}C_5H_{11}-$, $PhCH_2-$. A mono-potassium derivative of ethylene glycol, CH_2OHCH_2OK, prepared by reaction with potassium in liquid ammonia, may be converted to the dipotassium compound by heating the solid mono-salt.[1]

Reactions resulting in the formation of ethers are described by White, Morrison and Anderson.[11] Potassium dissolved in liquid ammonia is converted to potassium amide by the addition of ferric oxide (a rusty nail). Ethyl alcohol is added, when a white precipitate of potassium ethoxide is formed. On adding ethyl iodide a vigorous reaction occurs, the precipitate dissolves and a clear colourless solution is formed. On removing ammonia a 71% solution of diethyl ether is obtained. Ethyl *n*-butyl ether in 19% yield is prepared similarly by using *n*-butyl bromide in place of ethyl iodide; ethyl benzyl ether is formed in 81% yield by the addition of benzyl chloride to potassium ethoxide and many similar syntheses have been recorded.

The simple aliphatic ethers are not attacked by solutions of metals in liquid ammonia. If however the ether contains at least one aromatic group, cleavage of a carbon–oxygen bond occurs in most cases. The information given by Watt[1] on the cleavage of aromatic ethers by potassium in liquid ammonia at 20°C. is summarised in Table X.

TABLE X.- CLEAVAGE OF AROMATIC ETHERS BY POTASSIUM IN LIQUID AMMONIA AT 20°C.

Ether	Products Identified
Anisole	Phenol about 100%
Veratrole	Guaiacol, pyrocatechol
Propylveratrole	Probably 4–hydroxy–3–methoxy– and 4–methoxy–3–hydroxy–propylbenzenes
Dihydroeugenol	No cleavage of $-OCH_3$
Di*iso*eugenol methyl ether	Partial demethylation
Di*iso*eugenol	No cleavage of $-OCH_3$
Vanillin	No cleavage of $-OCH_3$*
Vanillic acid	No cleavage of $-OCH_3$
Egonol	No cleavage of $-OCH_3$
Dihydrosafrole	*p*–Hydroxyphenylpropane
Piperonylic acid	*m*–Hydroxybenzoic acid

*The aldehyde group is reduced to a primary alcohol group

Not many reactions of ketones with potassium in liquid ammonia have been studied,[1] but Schlubach[2] has prepared a potassium derivative, $C_7H_8O_2K$, by the action of potassium on dimethylpyrone in liquid ammonia.

Benzophenone diethylketal reacts with potassium in liquid ammonia at −33·5°C. to form potassium ethoxydiphenylmethide and potassium ethoxide: $Ph_2C(OEt)_2 + 2K \rightarrow Ph_2C(K)OEt + EtOK$; about 14·4% of the acetal is cleaved: $Ph_2C(OEt)_2 + 4K \rightarrow Ph_2CK_2 + 2EtOK$.

A deep blue-violet solution of a monopotassium derivative is obtained when one mole of benzil reacts with one g. atom of potassium in liquid ammonia; with two g. atoms of potassium a deep red solution and a precipitate are obtained. Neither the mono- nor the di-potassium derivatives are pure because some of the benzil reacts with liquid ammonia to form high-melting products containing nitrogen.

Benzophenoneimine reacts with potassium in liquid ammonia to form intensely red and very soluble products. There is up to 50% reduction to benzohydrylamine or benzophenone-benzohydrylamine.[1]

Acetophenone, PhCOMe, is reduced by potassium and *tert.*-butyl alcohol in liquid ammonia to ethylbenzene. If the reduction with potassium is started three hours after the addition of acetophenone to potassium *tert.*-butoxide in liquid ammonia, then only acetophenone is obtained. The carbinol, PhCHMeOH, is similarly reduced to 1–ethyl–1:4–*cyclo*hexadiene. The ketone, *o*–methoxyacetophenone, *o*–MeOC$_6$H$_4$COMe, is reduced in a few minutes by potassium and *tert.*-butyl alcohol in liquid ammonia to 6–ethyl–2–*cyclo*hexen–1–one and a syrup is formed which partially crystallises on storage and is probably a self-condensation product of *o*–methoxyacetophenone; some crude *o*–methoxyacetophenone is also present. If the solution of the original ketone is kept for 4hr. in the presence of potassium *tert.*-butoxide in liquid ammonia, before reducing with potassium, the product contains 6–ethyl–2–*cyclo*hexen–1–one together with a small amount of the methoxy compound, *o*–EtC$_6$H$_4$OMe, and a nonvolatile syrup which forms some crystals, the infrared spectra of which show no OH band at 3μ and no CO band at 6μ. The carbinol, *o*–MeOC$_6$H$_4$CHMeOH reduced with potassium in liquid ammonia containing *tert.*-butyl alcohol gives an oil which gives a low yield of two 2:4–dinitrophenylhydrazones, identical with the two derivatives of 6–ethyl–2–*cyclo*hexen–1–one.[12]

An account of the reactions of carbohydrates and related substances with alkali metal solutions in liquid ammonia is given by Watt.[1] A number of potassium salts have been prepared as intermediates in the synthesis of carbohydrate derivatives but not isolated: tetra-potassium *α*–methylmannoside, tripotassium monoacetoneglucose, monopotassium diacetoneglucose, monopotassium acetone methylrhamnoside, monopotassium 2:3–acetone methylrhamnopyranoside, octapotassium sucrose and monopotassium heptamethyl-*iso*sucrose.

Potassium and sucrose in liquid ammonia react rapidly at first until the formation of the di-potassium saccharide is completed; on addition of more potassium a slow reaction takes place and a white precipitate of a mixture of hexa– and hepta– potassium saccharide is formed. Probably some octa-potassium saccharide is formed. The polypotassium saccharide is almost insoluble in liquid ammonia and is highly reactive; when dry it inflames rapidly in air.[13]

Amagasa and Hori[14] have since prepared octabenzylsucrose from the above polypotassium saccharide and consider that the polypotassium saccharide contains octa-potassium saccharide.[14]

Diacetone glucose reacts with potassium in liquid ammonia to give a potassium salt, m.p. 150°C., which reacts with alkyl halides but does not form disaccharides when treated with acetohaloglucoses or diacetone–1–chloromannose.[1]

Starch and methylated starch form potassium salts when acted upon by potassium in liquid ammonia.[1]

Cellulose on treatment with alkali metals in liquid ammonia yields mono–, di–, or tri-alkali metal salts depending upon the amount of alkali metal used. The alkali salts are used to prepare cellulose ethers, esters, xanthates and cellulose monoamine.[1]

When lignin is treated with potassium in liquid ammonia, extensive demethylation occurs at –33·5°C. and at 20°C. and phenolic decomposition compounds are formed. Cellulose and carbohydrate fragments are also obtained. Whereas methylglucoside is not attacked, phenylglucoside is degraded to glucose and other decomposition products.[1]

Acid amides react with alkali metal solutions in liquid ammonia to form salts, hydrogen being liberated. The potassium salt obtained from acetamide reacts with ethyl bromide to give ethylacetamide. Ethylacetanilide is obtained in a similar manner from potassium, acetanilide, liquid ammonia and ethyl bromide.[11]

o–Formotoluide when treated with potassium in liquid ammonia yields

51% of indole.[1]

Urea reacts rapidly with the alkali metals in liquid ammonia to form mono-alkali salts and then more slowly to form the di-alkali salts.[1]

Proteins such as silk fibroin, casein, edestin and silk react readily with potassium in liquid ammonia to form hydrogen and ammonolytic products containing potassium.[1]

Nitrosobenzene reacts with potassium in liquid ammonia to form dipotassium phenylhydroxylamine: $C_6H_5NO + 2K \rightarrow C_6H_5N(K)OK$.[1]

Aniline reacts with potassium in liquid ammonia to give a monopotassium salt which on subsequent treatment with ethyl bromide yields mono-ethyl aniline with only traces of diethylaniline. Similarly diphenylamine reacts with potassium in liquid ammonia to give a potassium derivative from which ethyldiphenylamine may be prepared by further treatment with ethyl bromide.[11]

Hydrogen is evolved and the blue colour of potassium in liquid ammonia is discharged by the addition of pyrrole. The potassium salt has not been isolated in a crystalline form.[1]

Extensive reduction of carbazole occurs with potassium in liquid ammonia; the solution becomes intensely coloured and only a small amount of hydrogen is liberated.[1]

Piperonylic acid is converted to *m*-hydroxybenzoic acid by the action of potassium in liquid ammonia at −70°C. Dihydrosafrole is reduced under similar conditions to *p*-hydroxypropylbenzene. The coumaran ring in di*iso*eugenol and its methyl ether and the coumarone ring in egonal are ruptured by treatment with potassium in liquid ammonia at 20°C. The heterocyclic ring in *d,l*-epicatechin is not ruptured by potassium in liquid ammonia.[1]

Potassium in liquid ammonia reacts with sulphur compounds; use is made of this reaction to purify petroleum.[1]

Germane, GeH_4, reacts with potassium amide in liquid ammonia and the monopotassium salt, $KGeH_3$ is formed.[15] Triethylgermanyl, EtGeH, reacts with potassium in ethylamine to form potassium triethylgermanide, Et_3GeK, which is stable in liquid ammonia.[1]

The lead organo-compound, $(Ph_3Pb)_2$, is converted by potassium in liquid ammonia to the potassium salt, Ph_3PbK, which on further treatment with benzyl chloride forms triphenyl-benzyl lead.[1]

Potassium reacts with tributylboron, Bu_3B, in liquid ammonia according to the equation: $Bu_3B,NH_3 + K \rightarrow KNH_2BBu_3 + 0{\cdot}5H_2$. A similar reaction carried out in ethylamine instead of liquid ammonia does not yield the stoicheiometric amount of hydrogen.[16]

Organobismuth halide compounds react with potassium in liquid ammonia to give highly reactive, deep red R_2BiK compounds which decompose slowly to R_3Bi compounds but are sufficiently stable to react promptly with organohalides, *i.e.* RX compounds, to form unsymmetrical organobismuth compounds R_2RBi, and a water-soluble type, $R_2BiC_6H_4COOH$. The first reaction is represented by: $Ph_2BiI + 2K \rightarrow Ph_2BiK + KI$.[17]

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REACTIONS OF POTASSIUM WITH ORGANIC COMPOUNDS

The simple alkyls and aryls of potassium are prepared by treating the metal with a mercury alkyl or aryl, using light petroleum as a solvent for the mercury compound; on continued shaking of the reaction mixture a suspension of the organo-potassium compound is formed. For example when potassium in definite excess is treated with diethyl mercury in petroleum ether, ethyl potassium is formed. The reaction, $Et_2Hg + 2K \rightleftharpoons 2EtK + Hg$, is reversible, but with excess of potassium goes essentially to completion; in this case potassium amalgam is also formed.[1] Methyl potassium is obtained in a similar manner.[2] An immediate reaction occurs, as is shown by the formation of potassium amalgam, when potassium shavings in benzene are treated with diethyl mercury; a gas is given off and the benzene becomes warm. The mixture is stirred without heating for 48hr. On cooling to 7°C. and carbonating with carbon dioxide, a yield of 33% of benzoic acid and 14% of terephthalic acid with some phthalic acid is obtained. The gas evolved is chiefly ethane with small amounts of ethylene and hydrogen. The primary reaction is the formation of ethyl potassium which then reacts with benzene which is metalated to phenyl potassium: $C_6H_6 + EtK \rightarrow PhK + C_2H_6$. The isolation of phthalic and terephthalic acids on carbonation establishes the formation of the intermediate *o*– and *p*–dialkalibenzenes produced by self-metalation of phenyl potassium.[3] Phenyl potassium is also formed when potassium in benzene is stirred for 48hr. with di-*n*–butyl mercury; very little heat is evolved and the potassium compound is precipitated.[4] Phenyl potassium is also formed by treating lithium phenyl with potassium.[5]

The simple alkyls and aryls of potassium are colourless, solid, amorphous, non-volatile, salt-like compounds, insoluble in all solvents other than zinc ethyl in which they form conducting solutions. On heating, they decompose without melting. Potassium methyl, KCH_3, when heated from 100° to 300°C., decomposes according to the equation: $8KCH_3 \rightarrow 6CH_4 + K_2C_2 + 6K$. In their chemical properties, all the five alkali metal derivatives are very similar but their reactivity, particularly with halides and nitriles, is greatest for cæsium derivatives and least for lithium compounds, in the order: Cs>Rb>K>Na>Li>MgBr.[5,6] The stability of metal organo-compounds has also been discussed by Jaffé and Doak.[7]

Molecular hydrogen reacts with potassium phenyl at room temperature to form potassium hydride and benzene.[4] The rates of reduction for all the alkali metal phenyls are shown in Table XI.

The acetylides, KC_2H and K_2C_2, are formed by the action of acetylene on the heated metal or on its solution in liquid ammonia. The alkali metal acetylides are colourless, crystalline compounds, violently decomposed by water to potassium hydroxide and acetylene, and although stable in air when cold are readily oxidised when warmed.[5]

The potassium salt of phenylacetylene, $PhC \equiv CK$, is formed by the action of potassium on the hydrocarbon in ether solution. On carbonation the cor-

TABLE XI.- REDUCTION RATES OF ALKALI-METAL PHENYLS WITH MOLECULAR HYDROGEN

Compound	Average Time (hours) For Complete Reduction With H_2 at 100 lb.	Average Time (hours) For 90% Reduction, Pressure Slightly Above Atmospheric
PhLi	32·2	–
PhNa	0·5	1·9
PhK	–	0·54
PhRb	–	0·42
PhCs	–	0·2

responding acid is obtained: $PhC \equiv CK + CO_2 + H_2O \rightarrow PhC \equiv C.COOH$. From the measured rates of reaction of the alkali-metal phenylacetylenes with benzonitrile, it is found that the cæsium derivative is the most reactive and the lithium compound least so.[1]

Triphenylmethyl potassium, an intensely red solid, soluble in ether and benzene and in liquid ammonia, is obtained by displacement of hydrogen from triphenylmethane with potassium at 200°C.[8] When triphenylmethane is treated with potassium in liquid ammonia and methyl iodide is then added, the following reactions occur: $Ph_3CH + K \rightarrow Ph_3CK + \frac{1}{2}H_2$; $Ph_3CK + MeI \rightarrow Ph_3C.Me + KI$; $MeI + NH_3 \rightarrow MeNH_3I$; $MeNH_3I + Ph_3CK \rightarrow Ph_3CNH_2Me + KI$. By renewing the treatment with potassium followed by addition of more methyl iodide, a sufficient proportion of the by-product is converted to triphenylethane which is thus obtained in 85–94% yields.[8]

Compounds containing a carbon atom attached to a metal atom and to one or more aromatic nuclei or to a system of conjugate double links are coloured and may be prepared by the action of the metal on an organic halide, a mercury organic compound, a Grignard reagent or a mixed ether. Ziegler and Thielmann[9] have prepared potassium derivatives by shaking potassium powder or liquid sodium–potassium alloys with mixed ethers in dry ethyl ether at room temperature: $ROR' + 2K \rightarrow RK + KOR'$. The deeply coloured potassium compounds have not been isolated in the pure state but have been identified by conversion to known products. A deep-red, crystalline potassium derivative, $Ph_2CKCH{:}CPh_2$, sparingly soluble in ether, is formed from 1:1:3:3-tetraphenylallyl ethyl ether, $Ph_2COEt.CH{:}CPh_2$. Triphenylmethyl potassium is prepared from triphenylmethyl ethyl and triphenylmethyl phenyl ether. Benzhydryl ethyl ether and dibenzhydryl ether both give an intensely yellow potassium derivative, Ph_2CH_2K, sparingly soluble in ether. Benzophenonedimethylacetal, *a*:*a*-dimethoxydiphenylmethane, gives *a*-methoxydiphenylmethyl potassium, $Ph_2C(OMe)K$, as well as potassium methoxide; the former potassium derivative is a brownish yellow insoluble substance. Phenyl*iso*propylpotassium is prepared by the following reaction: $PhCMe_2OMe + 2K \rightarrow PhCKMe_2 + CH_3OK$. Diphenylmethylpotassium, Ph_2CHK, has been prepared from *sym.*-tetraphenylethane by cleavage with sodium–potassium alloy: $Ph_2CH.CHPh_2 + 2K \rightarrow 2Ph_2CHK$.[9]

The reactions represented by the following equations have been carried out with sodium–potassium alloy: $Ph_3COEt + NaK \rightarrow Ph_3CK$; $Ph_2CHOMe + NaK \rightarrow Ph_2CHK$; $Ph_2CHCHPh_2 + NaK \rightarrow Ph_2CHK$; $Ph_2C = CPh_2 + NaK \rightarrow Ph_2CKCKPh_2$. Potassium itself does not add on to tetraphenylethylene, nor does rubidium or cæsium, but sodium–potassium alloy and sodium–rubidium alloy give respectively potassium and rubidium derivatives, probably formed via the sodium compound. Steric hindrance associated with the larger atomic volumes of potassium, rubidium and cæsium is probably responsible for their non-reactivity.[1]

Durand[10] has observed that when drying ether with sodium, hydrogen is evolved even after long standing. An investigation carried out using various ethers and sodium–potassium alloy shows that the reaction with the alloy is much more vigorous, particularly in the cold.

Fluorenyl potassium, $(C_6H_4)CHK$, has been prepared by the direct action of the alkali metal on the hydrocarbon, as also has pentaphenyl*cyclo*pentadienyl potassium, $Ph\underline{C=CPh-C(PhK).CPh=C}Ph$. *cyclo*Pentadiene when treated with potassium metal yields $(C_5H_5K)_2$.[8]

Alkali metal alkyls can add to conjugated double bonds or to double bonds adjacent to a benzene nucleus. The potassium derivatives of dimethylphenylmethane, $PhCKMe_2$ and stilbene $(PhCH:)_2$ react to form an orange yellow compound, $PhCMe_2CHPhCHKPh$, soluble in ether. Coloured compounds are also formed with styrene, 1:1-diphenylethylene, anthracene and 2:3-dimethyl-1:3-butadiene, $(CH_2=CMe)_2$; the respective potassium derivatives are: $PhCHKCH_2CMe_2Ph$, $Ph_2CKCH_2CMe_2Ph$, $\underline{C_6H_4CH(CMe_2Ph)C_6H_4C}HK$, $CH_2=CMeCKMeCH_2CMe_2Ph$. No addition compound is formed with *cyclo*hexene. The potassium derivative of triphenylmethane, Ph_3CK, shows little tendency to add. Substances of very high molecular weight may be obtained by addition of potassium alkyls. If for instance an alkyl, RK, reacts with a butadiene, it forms a potassium alkyl, $RCH_2KCH=CH_2$, which can add another butadiene molecule, and the reaction continues in this way until stopped by atmospheric oxygen, by traces of impurity or because the molecules finally become so large that they react sluggishly.[11]

Phenyl*iso*propyl potassium, which is dark red, reacts with butadiene to give unsaturated polymerisation products containing up to 10 molecules of butadiene.[12]

The action of potassium on 1:1:6:6-tetraphenylhexadiene-1:5 is represented by the equation: $Ph_2C=CHCH_2-CH_2CH=CPh_2 + 2K \rightarrow 2Ph_2C=CHCH_2K$. Similarly, 1:2-dibiphenylylethane reacts with potassium: $PhC_6H_4CH_2-CH_2-C_6H_4Ph + 2K \rightarrow 2Ph.C_6H_4.CH_2K$. The action of potassium on 1:1:4:4-tetraphenylbutene-1 results in cleavage and the formation of two potassium derivatives: $Ph_2C=CHCH_2CHPh_2 + 2K \rightarrow Ph_2CHK + Ph_2C=CHCH_2K$.[6]

Neither a definite alkali metal compound nor any decomposition products have been obtained which would indicate a reaction between potassium and benzene.[8]

Dipotassium compounds are formed by the direct action of potassium at a double carbon link, $>C=C< + 2K \rightarrow >CK.CK<$ provided that the $>C=C<$ group is attached to an aryl group or at least to two conjugated double linkages.[9]

Potassium reacts with ethyl acetate in dry ether to form the potassium derivative $CH_2:C(OK)OEt$, acidic substances and neutral compounds. Traces of hydrogen are evolved and it appears that the liberated hydrogen reduces a portion of the potassium derivative. Intermediate compounds more readily reducible than the potassium derivative give rise to hydrocarbons; a certain proportion of ethers is also formed. When potassium is replaced by sodium, no hydrocarbons are formed.[13]

The action of potassium on esters of the fatty acids has been studied by Scheibler and Emden.[14] Ethyl dibenzylacetate, $(PhCH_2)_2CHCO_2Et$, when treated with potassium in dry ether solution, gives $(PhCH_2)_2CHC(OK):C(OK)-CH(CH_2Ph)_2$. Other esters have been treated similarly.

The diketone, benzil, gives a dipotassium derivative when treated with potassium: $PhCO.COPh + 2K \rightarrow PhC(OK)=C(OK)Ph$. Compounds such as Ph_2COK, prepared by treating the ketone with sticks of alkali metal in an inert organic solvent, are described as "metal ketyls".

The properties of alkali metal alkoxides have been investigated by Brun[15] and measurements made of the current produced when potassium is dissolved in methyl and ethyl alcohols, of the electrolytic decomposition of the alkoxides, and of the ionic mobilities and the degree of dissociation of the compounds. The results indicate that the alkoxides are not true organic compounds but resemble the metallic hydroxides. Cordier[16] has calculated the solvation of potassium ions in methyl and ethyl alcohols and in acetone and ethyl acetate from published data on the apparent molecular volumes. Trimethylsilanol reacts more vigorously with potassium at 0–3°C. than does the carbinol.[17]

Dehydrotetrachloro-*p*-cresol, a radical with monovalent oxygen, reacts with potassium powder in benzene to give a product which when dissolved in water and acidified yields phenolic products consisting partly of tetrachloro-*p*-cresol.[18]

Potassium derivatives of organic compounds containing the NH-group are described by Shah and Pishavikar.[19] The amide is treated with potassium in boiling toluene and potassium derivatives of the following amides are obtained as microcrystalline compounds, insoluble in organic solvents: *m*-MeC_6H_4NHAc, AcNHMe, Ac_2NH, $(PhNH)_2CO$, $(PhNHCO)_2$. Under the same conditions the following compounds do not appear to give potassium derivatives: Ph_2NH, PhNHMe, PhNHEt, $PhNHCH_2Ph$, carbazole and indole.

Hydrocarbon substituted pyrimidines and pyridines are obtained when mononitriles and monoacetylenes are allowed to react in the presence of catalytic quantities of potassium at a pressure of 100–300lb. per sq.in. at 125°–225°C. for several hours. Thus acetonitrile and acetylene in the presence of potassium give 2:4-dimethylpyrimidine. Similarly 2:4-di*iso*propylpyrimidine and 2:4-diphenylpyrimidine are prepared from the appropriate nitrile and acetylene. In the latter case a shorter time of heating results in the formation of some 2-phenylpyridine as well. Acetonitrile, butylacetylene, CH⋮CBu and potassium give dimethylbutylpyrimidine.[20]

The action of potassium and alcohols on some monobenzenoid compounds has been investigated by Birch *et al.*[21] Potassium is added in small pieces over 45–60min. with vigorous stirring to a solution of the benzenoid compound in alcohol kept at 50°–60°C. Dihydroderivatives are formed, with yields given in Table XII.

TABLE XII.-ACTION OF POTASSIUM AND ALCOHOLS ON BENZENOID COMPOUNDS

Benzenoid Compound	Alcohol	% Yield of Dihydroderivative
PhOMe	EtOH	35
	BuOH	42
o-$MeOC_6H_4Me$	EtOH	10
m-$MeOC_6H_4Me$	EtOH	27
	BuOH	27
	i-PrOH	19
	MeOH	19
	i-AmOH (85–95°C.)	21·6
	i-AmOH (130°C.)	18·3
p-$MeOC_6H_4Me$	EtOH	36
	BuOH	36
$PhNMe_2$	EtOH	10
PhMe	EtOH	43
2:6-$Me_2C_6H_3OMe$	EtOH	2·6
2:4-$Me_2C_6H_3OMe$	EtOH	11·0
3:5-$Me_2C_6H_3OMe$	EtOH	7·6

The order of ease of reduction is anisole > dimethylaniline > toluene. Sodium and ethyl alcohol do not reduce *m*-$MeOC_6H_4Me$.

The reactions of halides with potassium-sodium alloy, listed in Table XIII, are described by Hückel, Kraemer and Thiele.[22]

TABLE XIII.- REACTIONS OF ORGANIC HALIDES WITH SODIUM-POTASSIUM ALLOY

Halide	Solvent	Products
MeBr	Xylene	C_2H_6
EtBr	Xylene	C_2H_6, C_2H_4, C_4H_{10}
PrBr	Xylene	C_3H_8, C_3H_6, C_6H_{14}
MeCl	Xylene	No reaction
EtCl	Xylene	C_2H_6, C_2H_4, C_4H_{10}
Me_2CHCl	Xylene	C_3H_8, C_3H_6, C_6H_{14}
Me_2CHBr	Xylene	C_3H_8, C_3H_6
Me_2CHBr	Decalin	C_3H_8, C_3H_6
Me_2CHBr	Benzene	C_3H_8, C_3H_6
MeBr + EtBr	Benzene	C_2H_6, C_2H_4, C_3H_8, C_4H_{10}
MeBr + PrBr	Benzene	C_2H_6, C_3H_6, C_4H_{10}, C_6H_{14}
MeBr + Me_2CHBr	Benzene	C_2H_6, C_3H_6, *iso*-C_4H_{10}

Explosive reactions with mixtures of potassium and halogen-organo compounds are described by Staudinger,[23] Lenze and Metz[24] and Cueilleron.[25] Explosive reactions occur when 1:1:2:2-tetra- and penta-chloroethane, or tri- and tetra-bromoethane are allowed to stand at rest at room temperature with potassium. Under the same conditions with trichloromethane, 1:2-dichloro- and 1:2-dibromo-ethane and 1:2-di-, tri- and tetrachloroethylene, only evolution of gas occurs. Carbon tetrachloride, monobromo- and monochloro-benzene and benzyl chloride are not essentially affected when allowed to stand quite still with potassium at room temperature. A very strong explosion has been observed when tetrachloro- and tetrabromo- methane are heated at the relatively low temperature of 65–70°C. for a short time with potassium. The fact that an explosive reaction does not occur at 60°C. indicates that it is liquid potassium (m.p. 62.5°C.) which is responsible for the reaction. Liquid sodium-potassium alloys are more reactive than sodium and potassium, probably because thay are in the liquid state.

Dichloroethylene, dibromo- and dichloro-ethane and potassium mixtures are also sensitive to temperature although to a smaller extent.

In Table XIV, values are given (in arabic figures) for the minimum percussion impulse (m. × kg.) required to produce an explosive effect, when halogen organo- compounds are mixed with potassium; the figures in brackets refer to the number of explosions for five tests and the roman numbers to the strength of the explosion on the scale: I, very weak explosion, II, weak explosion, III, moderately strong, IV, strong and V very strong explosion.

The reaction with carbon tetrachloride is represented by the equation: $4K + CCl_4 \rightarrow 4KCl + C + 390{\cdot}77$ kg.-cal. According to Staudinger[23] the explosive nature of mixtures of the alkali metals and halogen organo-compounds is due to the formation of a labile intermediate compound, the disintegration of which initiates the explosion of the whole system. It is possible that the reaction does not proceed directly to the final products but takes place in a series of steps, probably chain reactions, whereby explosive substances such as mono- or dichloro- acetylene are formed; as these are very labile they can bring about the explosive decomposition of the whole system. The power of the explosions is in the order: NaK > K > Na > Li > Ba.[24]

TABLE XIV.- SENSITIVITY TO SHOCK (BY MEANS OF A FALL-HAMMER) FOR MIXTURES OF POTASSIUM WITH HALOGEN-SUBSTITUTED METHANES

Halogen Compound	Sensitivity to Shock
	m × kg.
CH_3Cl	0·3 (5) II
CH_2Cl_2	0·02 (5) III
$CHCl_3$	0·01 (5) V
CCl_4	0·005 (5) V
$CHBr_3$	0·005 (5) V
CBr_4	0·005 (5) V
CH_2I_2	0·02 (5) III
CHI_3	0·02 (5) IV

Potassium heated with tetrachloroethylene produces explosions at 205°–210°F. whether oxide scale is present or absent; no explosion occurs when sodium is substituted for potassium.[26]

Chemical reactions in the decomposition of organic compounds with potassium have been discussed by Kainz and Resch.[27] Low results in the determination of halides have formerly been attributed to the formation of by-products assumed to be soluble in water but capable of reacting with iodine. In fact, very finely divided carbon is formed, a part of which combines with potassium to form potassium acetylide, and this yields acetylene when the melt is decomposed with water. Probably potassium also withdraws oxygen from the compound and hydrogen is liberated. Organic compounds containing nitrogen form potassium cyanide, and those containing sulphur and halogens form water soluble compounds which ionize when in the lowest state of oxidation.

Schwarz[28] considers that oil deposits in the neighbourhood of potassium salts are acted upon by alpha rays from the potassium with the result that lower and higher boiling constituents of the oil are produced at the expense of those of medium boiling point. The compounds formed are benzene, naphthenes, acids and asphalt, and optical activity is caused. It is estimated that alpha rays from 10 kg. of potassium would take 300,000 years to produce sufficient heat to crack one gram molecule of hexane.

Potassium dissolves in ethylene glycol dimethyl ether to form an intensely blue, electrically conducting solution.[29] The solution resembles a liquid ammonia solution of potassium.

When monochlorosilane, SiH_3Cl, is brought into contact with potassium, previously distilled in vacuo, the surface of the potassium becomes blue at once and a protective film is formed. After heating several hours up to 300°C., a deep-seated reaction occurs and complete decomposition of the silicon compound results. Among the non-volatile products are silicon, potassium hydride and potassium chloride; the residual gas is pure hydrogen.[30]

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SECTION XLVI

POTASSIUM ALLOYS

By Mrs. F. DICKINSON

Alloys of potassium with lithium and sodium have already been described (see Part 1, pages 95,548 "Lithium Alloys" and "Sodium Alloys").

The existence of the intermetallic compound KRb in the vapour state has been demonstrated by absorption spectra.[1]

Rinck has studied the potassium–rudibium system and found the elements to be completely miscible in the solid state. The solidus and liquidus are close together with a flattened minimum at 32·8°C. corresponding to a composition of K + 2Rb, but the solid is believed to be made up of mixed crystals.[2] According to Goria[3] the thermal diagram of the above system shows a limited range of solid solutions; no compounds are indicated but there is a eutectic at 34°C. and 15% of potassium. The compositions at minima in binary systems of the solid solution type have been determined by Hara[4] for twelve completely isomorphous bimetallic systems of which one is the potassium–rubidium system. The composition at the minimum freezing point corresponds to the formula Rb_2K. Böhm and Klemm from thermal analysis and *X*-ray studies of the potassium–rubidium system agree with Rinck that the system is completely miscible.[5] An account of the experimental data for systems of the alkali metals is also given by Klemm.[6] The phase diagram[7] is shown in Fig. 1.

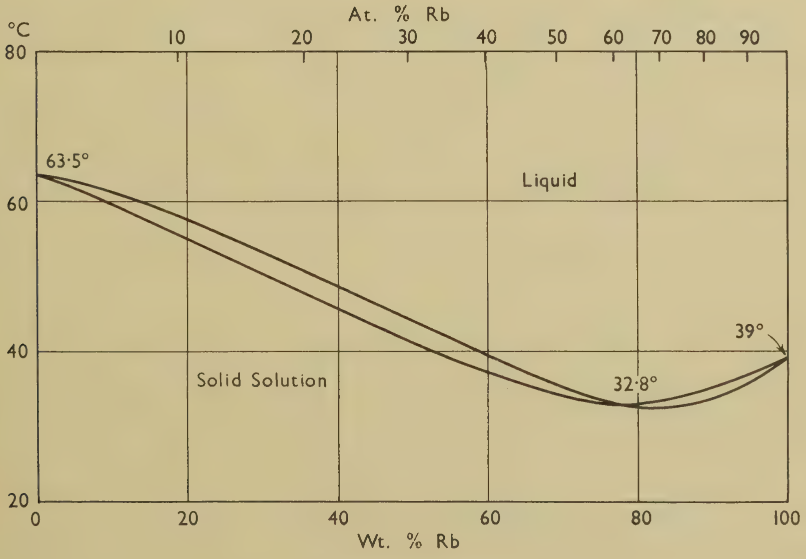

FIG. 1. THE SYSTEM K–Rb

Refs. p. 1616

The melting points of potassium and rubidium, the heats of mixing in the liquid solution, U (l), and the solid solution, U (s) and the concentrations of the liquid and solid solutions have been used by Geguzin and Pines[8] to predict the shapes of the liquidus and solidus curves for simple binary systems. If T_A, T_B are the melting points of the pure components, U_0^1 and U_0^2 the energies of mixing in the liquid and solid phases, k the Boltzmann's constant, q the entropy change, then at the point of equal concentrations:

$$x_0 = y_0 = 0{\cdot}5 \left[1 - \frac{kq(T_B - T_A)}{U_0^1 - U_0^2}\right]$$

and

$$T = Tm = T_A - \frac{U_0^1 - U_0^2 . x_0^2}{kq}$$

where Tm is the temperature at which the mixture melts. From the above relationships

$$Tm = T_A - (T_B - T_A)\frac{x_0^2}{1 - 2x_0} .$$

For the system rubidium–potassium, T_A = 312°C., T_B = 338·5°C.; with the aid of experimental values of x_0, the above expression has been used to calculate Tm which is 301·5°T. The experimental value is 305·6°T.

A theoretical procedure for the calculation of elastic constants of binary solid solutions with a cubic lattice, e.g. the potassium–rubidium system, is described by Orlov.[9]

An alloy containing 55% of potassium and 45% of rubidium, solidifying initially at 45°C., finally at 42°C., has been examined by X-ray methods. The side of the body-centred cubic lattice, a, is 5·42 A.[10]

In connection with their work on the cohesion of alloys, Henry and Raynor[11] give calculations showing that, for the alloys of the alkali metals, solid solution formation is limited in all the possible systems except potassium–rubidium, potassium–cæsium and rubidium–cæsium, for which extensive solid solutions exist. The relative magnitude of the liquidus depression in the potassium–rubidium system is accounted for.

The electrical resistance of potassium–rubidium alloys and the relationship to the composition and temperature of the alloys are given by Guertler.[12] Electrical resistance data at low temperatures, from 4·2 to 70°K., are given for potassium–rubidium alloys and the experimental technique is described in detail; the effect of impurities has also been examined. The thermoelectric force of potassium–rubidium alloys containing 0·5, 8 and 13 at.-% of rubidium has been measured against lead over the temperature range 4·2°K. to about 70°K.[13,14]

The potassium–cæsium system has been studied by Goria[15] and Rinck.[16] A series of solid solutions is formed and there is a eutectic at −39°C. at a composition corresponding to the formula KCs; conductivity measurements show no compound formation, the composition KCs being a mixture.[16] Goria's value for the eutectic temperature, −45°C., is attributed by Rinck to the fact that the alloys were prepared in an inert atmosphere and not in a vacuum. The eutectic temperature calculated by Geguzin and Pines from the m.p. of the two metals, the heats of mixing in the liquid and solid solutions and the concentrations of the liquid and solid solutions is 237·4°K.[8] Distortion energy data have been calculated by Heumann for the potassium–cæsium system, based on simple lattice models; in spite of large volume differences, distortion energies are small and permit the existence of all possible solid solutions.[17] Henry and Raynor,[11] from their work on the cohesion of alloys, propose a theory which predicts the existence of extensive solid solutions for the potassium–caesium system and accounts for the relative magnitudes of the liquidus depression in the system.

Photoelectric studies have been made of potassium films deposited on a freshly evaporated silver surface.[18]

Potassium auride, KAu_2, is prepared by heating gold with excess of potassium in vacuo at 310°C. This compound, violet in colour, is stable over a limited range only and if the heating at 310°C. is prolonged or if the temperature is raised to 320–330°C. the compound KAu_4 is formed. This is olive green, stable in air, and brittle; when heated at 690°C. in vacuo it loses most of its potassium. The violet compound is also brittle and reacts slightly with air. The densities of several potassium–gold alloys and *X*-ray spectra for the above two compounds are given. Potassium is not appreciably soluble in gold at high temperatures.[19]

The spatial compression of potassium alloyed with gold has been studied by Biltz *et al.*[20] The space occupied by the alkali metals in gold alloys is much less than that occupied by the pure metals; this is considered to be due to compression because of the great differences in density. It has been shown that the molecular volume increment due to the addition of one atom of potassium to gold is 23, whereas in mercury and graphite alloys with potassium the increment is 25.

Liquid potassium and liquid magnesium are practically insoluble in each other.[21] The phase diagram[7] is shown in Fig. 2.

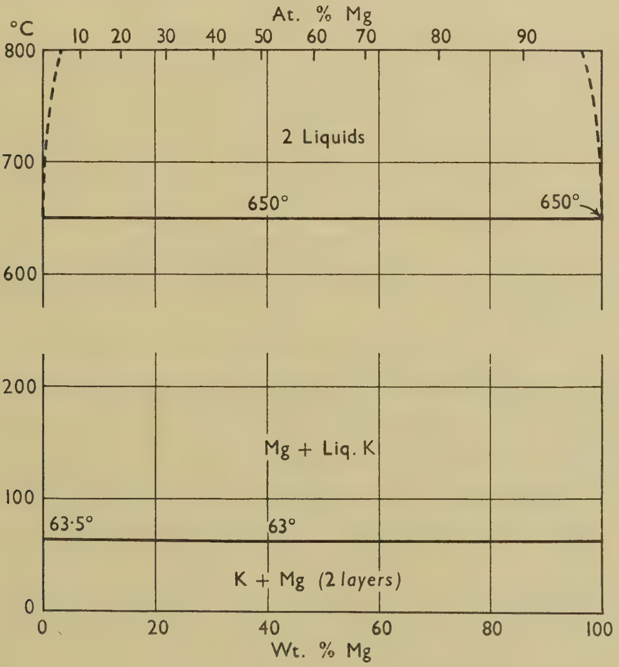

FIG. 2. THE SYSTEM K–Mg

The phase diagram given for the potassium–zinc system[7] and shown in Fig. 3 throws doubt upon the composition KZn_{12}. Ketelaar[22] refers to the compound as KZn_{13} as also do Zintl and Haucke.[23,24] The alloy is a crystalline cubic compound; the side of the lattice is given as 12·33 A.,[22] 12·36 A.[23 24] There are 112 atoms in the unit cell, and the alkali metal atom is surrounded by 24 equally distant zinc atoms. Zintl and Haucke[24] give powder diagram data.

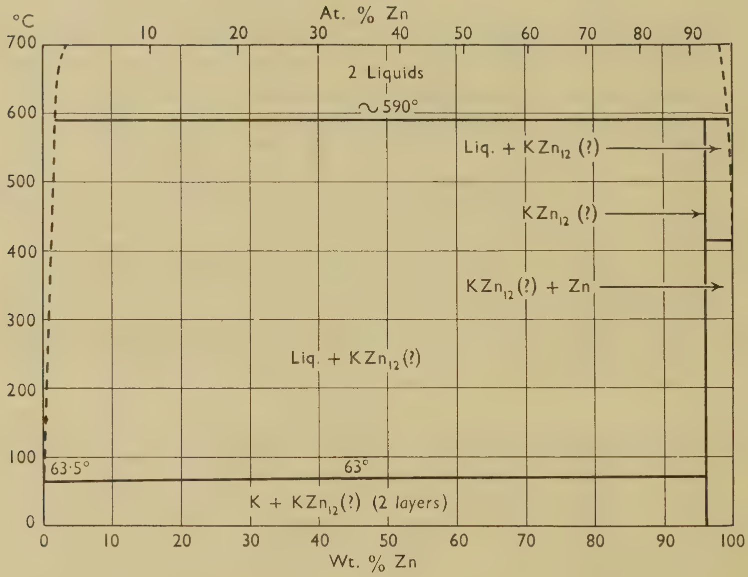

FIG. 3. THE SYSTEM K–Zn

The electromotive behaviour of potassium–zinc alloys has been studied by Kremann and Mehr.[25]

The solubility of potassium in gallium at 32°C. is about 4×10^{-6} wt.-%: the e.m.f. of the solution is 0·76 V.[26]

The phase diagram for the potassium–cadmium system,[7] Fig. 4, indicates the presence of the compounds Cd_7K and $Cd_{12}K$. According to Hansen[21] the composition $Cd_{12}K$ might be $Cd_{11}K$ since the difference in potassium content would only be 0·25%. The e.m.f./composition curve of Kremann and Mehr[25] does not establish conclusively the composition of this compound. Ketelaar[22] and Zintl and Haucke[23,24] describe the compound as $Cd_{13}K$, and the latter workers have extracted it as a crystalline alloy from high-potassium–zinc alloys with liquid ammonia. From *X*-ray data, density and analytical data the formula is found to be quite definitely $Cd_{13}K$, and not $Cd_{12}K$ or $Cd_{11}K$. It is a crystalline cubic compound with a lattice side a = 13·78 A.[22] [22] or 13·77 A.[23,24] with 112 atoms in the unit cell and the alkali atom surrounded by 24 equally distant cadmium atoms.[24]

The phase diagram for the potassium–mercury system shows the presence of the following compounds: Hg_8K, Hg_4K, Hg_3K, Hg_2K, HgK;[7,21] see Fig. 5 (page 1602).

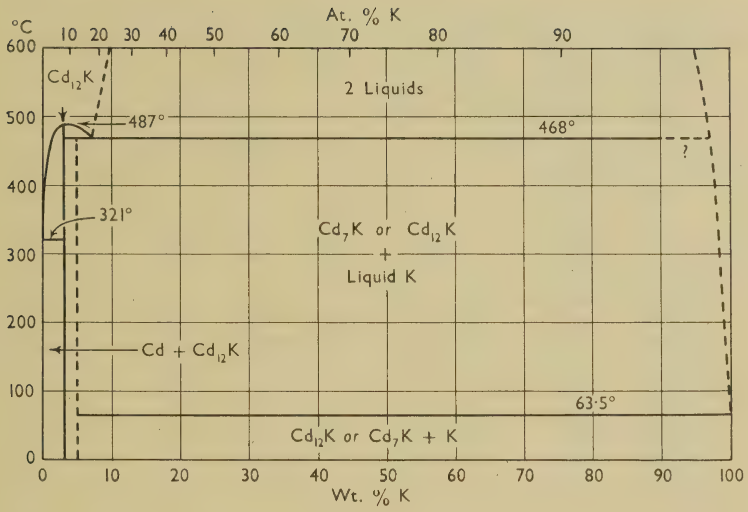

FIG. 4. THE SYSTEM Cd-K

The freezing points of the compounds are: Hg_8K, 70°C.; Hg_4K, 182°C.; Hg_3K, 201°C.; Hg_2K, 278°C.; HgK, 178°C.[21] The following formulae and melting points are given by Grube:[27] Hg_9K, 70°C.; Hg_9K_2, 173°C.; $Hg_{18}K_5$, 194°C,; Hg_7K_2, 197°C. (decomp.); Hg_3K, 204°C.; Hg_2K, 279°C. (decomp.); HgK, 178°C.

Zvyagintsev[28] has shown that it is possible to predict nearly all the binary intermetallic compounds observed in the system potassium–mercury by using the ionization potentials of the components as already described (in Part 1, page 576) for sodium–mercury compounds.

Klemm[29] describes the methods available for the detection of intermetallic compounds, *i.e.* *X*-ray investigations, thermal expansion by dilatometric methods, determination of electrical resistance as a function of temperature and the determination of magnetic properties as a function of the concentration and temperature. Equilibrium diagrams are given by Klemm for the alkali amalgams.

An investigation of the potassium–mercury system by *X*-ray diffraction is described by Duwell.[30]

The e.m.f. of cells in which the reaction is the transfer of potassium from an amalgam of higher to one of lower concentration have been determined at various temperatures and concentrations.[31] Kubaschewski and Catterall[32] use e.m.f. data obtained by Bent and Gilfillan,[31] Armbruster and Crenshaw,[33] and by Shibata and Oda[34] to obtain the partial heat of solution $\Delta\bar{H}_{K}-$, the partial entropy of solution $\Delta\bar{S}_{K}-$ and the integral heat of solution, $\Delta H_{liq.}$ given in Table I. The partial molal heat and entropy of solution and the heat of fusion of potassium have been used to calculate the partial

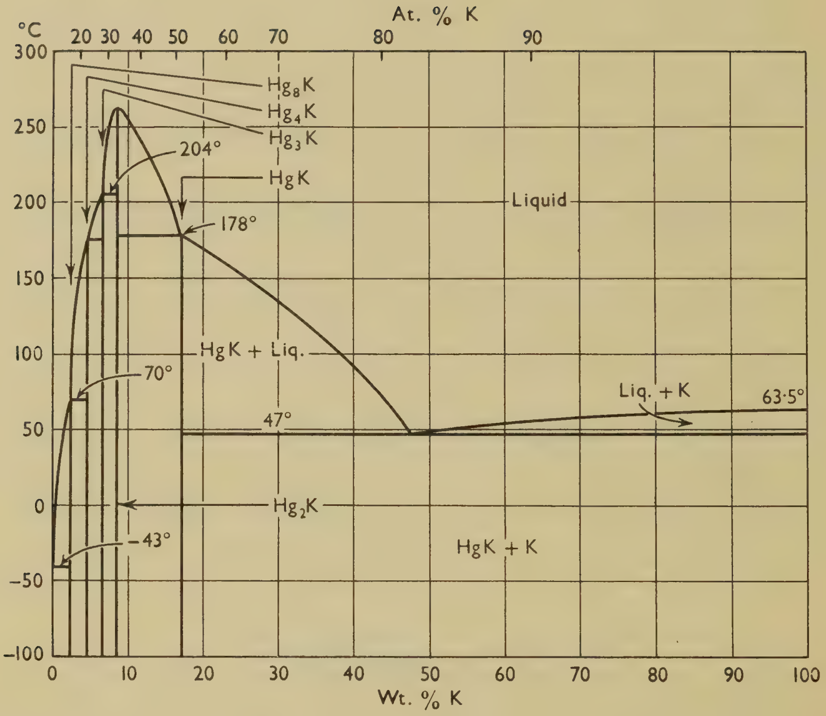

FIG. 5. THE SYSTEM Hg–K

free energy, $\Delta\bar{G}_K$ at 600°K. from data obtained by Vierk and Hauffe[35] for the e.m.f. of cells, K (liq.)/K^+ in glass/K–Hg (liq.) where alloys in the concentration range N_K = 0·26 to 0·99 have been used. Pedder and Barratt[36] have determined the partial vapour pressures of each of the constituents of potassium amalgam by a dynamic method at temperatures between 250°C. and 400°C. The partial vapour pressures of mercury for alloys containing up to 42·8 mol.-% K have been measured at 300°C. and the results obtained are in good agreement with those of Miller[37] who has used a static method for alloys containing 5–32 mol.-% K over the temperature range 184°C. to 445°C. Below 8 mol.-% K the partial molar heat content of the solvent, mercury, is zero while above this concentration it becomes negative. The very low partial pressures of potassium found by Pedder and Barratt are believed to indicate the presence of almost undissociated compounds in the liquid amalgam. From experiments carried out at 387·5°C. with amalgams containing 41 to 63 mol.-% K it would appear that there is a considerable amount of a potassium–mercury compound present in the vapour, probably HgK. The small activities of potassium in amalgams containing less than 45 mol.-% K indicate that the more complex compounds are relatively non-volatile. Lumsden[38] does not consider that this is true. Kubaschewski and Catterall[32] point out that the partial free energies, $\Delta\bar{G}_K$, obtained from Pedder and

Barratt's data do not agree with those of Vierk and Hauffe and that this is due to experimental error in the former determinations of P_K. The values given for the partial free energies, $\Delta\bar{G}_K$, at 600°K. shown in Table I are from the data of Vierk and Hauffe. The values for $\Delta\bar{G}_{Hg}$ are mean values from the results of Miller, Pedder and Barratt, and Vierk and Hauffe. According to Miller the solutions deviate from Raoult's Law more than any others so far observed.

TABLE I.- THERMOCHEMICAL DATA FOR LIQUID POTASSIUM-MERCURY ALLOYS

N_K	$\Delta\bar{H}_K$ 298°K.	$\Delta\bar{S}_K$ 298°K.	ΔH liq.	ΔV_{573}	$\Delta\bar{G}_K$ 600°K.	$\Delta\bar{G}_{Hg}$ 600°K.
0·001	−26,365	−1·185			(−25,210)	
0·005	−26,220	−4·40			(−23,140)	
0·01	−26,080	−6·00	−270		(−22,040)	
0·02	−25,750	−7·70	−520		(−20,700)	
0·02	−25,750	−7·70	−520		(−20,700)	
0·077			−1,350		(−16,200)	
0·10			(−1,470)	(−0·12)	(−15,050)	−500
0·20				−0·193	−10,700	−1,400
0·25				−0·215	−8,800	−2,050
0·33				−0·243	−5,500	−3,400
0·40				−0·252	−3,250	−4,600
0·50				−0·245	−1,570	−5,900
0·60				−0·205	−800	−6,700
0·70				−0·158	−460	−7,400
0·80			(−1,550)	−0·109	−275	−8,150
0·90			(−800)	−0·056	−130	−9,000

$\Delta\bar{H}_K$, $\Delta\bar{G}_K$, $\Delta\bar{G}_{Hg}$, the partial heat of solution and partial free energy are defined as the change in heat content and free energy respectively when 1 g.-atom of the metal is assimilated by a (theoretically) infinite amount of an alloy of constant composition N_K or N_{Hg} as the case may be. Both are expressed in calories. ΔH liq. refers to the integral heat of solution when N_K g.-atoms of liquid potassium combine with $(1 - N_K)$ g.-atoms of liquid mercury to give 1 g. atom of liquid alloy; the results are expressed as calories per g.-atom. The data given in column 4 agree approximately with those obtained calorimetrically by Kawakami[39] at 110°C. $\Delta\bar{S}_K$ is expressed as calories per degree when 1 g. atom of potassium is assimilated by a theoretically infinite amount of an alloy of constant composition N_K. ΔV_{573} refers to the volume change on formation at 300°C. and is equal to $(V \text{ alloy} - \Sigma V \text{ metals})/\Sigma V$ metals at 300°C. The specific volumes of fused potassium–mercury alloys of potassium concentrations 0–100% have been measured through a temperature range of 290°–380°C. by Degenkolbe and Sauerwald.[40]

Kubaschewski and Catterall[32] give thermochemical data for the solid compounds of potassium and mercury, which they list as $Hg_{12}K$?, Hg_9K, Hg_4K, Hg_3K, Hg_2K and HgK. There is some doubt as to the composition of the compound richest in mercury, but data are given for $Hg_{12}K$ and an alternative calculation has been made for Hg_9K. The values selected for the heats of formation in Table II are confirmed within the limits of accuracy of the method used by values derived from measurements of the dissociation pressures. Poindexter[41] has measured the vapour pressures of potassium amalgams of concentrations $HgK_{0\cdot195}$ to $HgK_{0\cdot094}$ near room temperature, and obtained approximately straight lines for the plot of p versus $1/T$. The heats of reaction are about 25,500 g.-cal. per g.mole.

The relation between the free and internal energy changes are discussed by the author. Gerke[42] has found the free energy of potassium in the alloy Hg_5K to be −24,200 g.-cal. per g.mole.

The entropies of formation, $\Delta S_{sol.}$, given in Table II have been obtained by Kubaschewski and Catterall[32] from the data of Bent and Gilfillan.[31] Poindexter's data show clearly that ΔS_{298} is negative.

TABLE II.- THERMOCHEMICAL DATA FOR SOLID COMPOUNDS OF MERCURY AND POTASSIUM

N_K	$\Delta H_{sol.}$	$\Delta S_{sol.}$	ΔV_{298}
0·077	(−2500)	(−2·8)	
0·1	−3300	(−3·6)	−0·13
0·2	−4600		−0·20
0·25	−5200		−0·23
0·33	−6100		−0·25
0·5	−5900		−0·26

$\Delta H_{sol.}$ is expressed as g.-cal. per g.atom, *i.e.* N_K g.atoms of K and $(1 - N_K)$ g.atoms of Hg; $\Delta S_{sol.}$ as g.-cal. per degree/g.atom.

Roeder and Morawietz[43] have recently investigated the composition of the vapour above mercury-potassium melts by measuring the total pressure, analysing the distillate and determining molecular weights. The behaviour of the vapour at temperatures below 250°C. can be ascribed to the presence of K_3Hg molecules. At temperatures above 250°C., compounds containing a lower potassium content appear. The activities of the atom components are calculated from mass-action constants and agree with the results of e.m.f. measurements and obey the Duhem–Margules equation. Energies and entropies are calculated from the temperature coefficient of the activities. Vapour pressure curves for pure potassium and mercury are given and the heat of evaporation of the alloy system reported as a function of composition.

Halban[44,45] has shown that vapour-pressure abnormalities occur in capillary-active amalgams. Measurements of the absorption of resonant light, 2537 A., show a vapour-pressure lowering of 69% but when the mercury is agitated, so that the concentration of the solute is kept uniform throughout, the vapour pressure of these dilute amalgams rises to that of mercury. Halban states that if a solution has a smaller surface tension than the solvent, the solute is adsorbed at the surface.

An account of the literature on the electrical properties of alkali-metal amalgams up to 1925 is given by Schulze.[46]

Molten potassium alloys have been electrolysed in tubes of small bore which are subsequently broken and different portions are analysed. Potassium amalgams behave similarly to the corresponding sodium amalgams (see Part 1) except that the increase in concentration of potassium at the cathode end of the tube is about twice as great, due partly to the fact that potassium is more strongly electropositive and partly to its larger atomic volume.[47] Le Blanc and Jäckh[48] and Skaupy,[49] Springer and Frena[50] Kremann, Vogrin and Scheibel[51] have studied concentration changes in dilute alkali metal amalgams in electrolysis. In amalgams containing up to 2·5% K, potassium moves to the anode; with higher concentrations to the cathode. The transference numbers towards the anode first increase, then decrease, pass through zero at 2·5% K, then change sign and steadily increase.

The transference and distribution of the components of metal alloys in an electric field have been described by Drakin.[52] When an electric current passes for a short time through a metallic phase before the back diffusion becomes noticeable, the "transference number" is $mF/It = Dc(V_1 - V_2)F^2p/RT$, where F is the faraday, m is the number of g.atoms transferred in time t by current I, D is the diffusion coefficient, c the concentration, p the electrical resistivity and V_1 and V_2 the average charges of "solvent" and "solute" ions respectively *i.e.* the number of free electrons originating from a component of the alloy/the total number of atoms of this component. In the system Hg–K, $V_1 - V_2 = 0{\cdot}036$. In the steady state $\ln(C_a/C_c) = E/T$, where E is the potential difference between the electrodes and T is the absolute temperature. This equation is confirmed by the experimental data of Le Blanc and Jäckh.

The wedge effect observed at potassium amalgam–electrolyte surfaces between the amalgam and glass at a specific minimum potential is considered to be due largely to electro-osmotic forces.[53].

Nakamura[54] has studied the formation of crystals during electrolysis of a saturated solution of potassium chloride at various current densities, with and without stirring the cathodic mercury. The times required for the separation of amalgam crystals on the amalgam (TA) and for the evolution of hydrogen gas (TH) are similar at current densities higher than 1·5–5 amp./sq. dm. With lower current densities TH is noticeably longer than TA. When electrolysis is carried out with stirring of the mercury cathode, the relation between TA and the average amalgam concentration is quite similar to the solubility curve; without stirring TA is noticeably longer for potassium amalgam than for sodium amalgam which is considered to be due to supersaturation as well as rather vigorous eddy movement in potassium amalgam. Pyramidal crystals are obtained from very high supersaturated states. Cubic crystals are also formed. The presence of vanadium, aluminium and magnesium ions promotes crystal formation.

The electrical conductivities of potassium amalgam have been determined by a number of workers.[55-58] The results given in Table III are those of Booshariwalla, Paranjpe and Prasad.[58]

TABLE III.- ELECTRICAL CONDUCTIVITY OF POTASSIUM AMALGAM AT 30°C.

Wt.-% K	Resistivity of Amalgam × 10^{-6}	Specific Conductivity of Amalgam × 10^4
0·0100	97·18	1·0290
0·0211	97·77	1·0228
0·0407	98·63	1·0139
0·0413	98·79	1·0122
0·0434	98·33	1·0179
0·0513	98·49	1·0153
0·0612	99·31	1·0068
0·0776	99·59	1·0041
0·0907	100·40	0·9960
0·0938	99·10	1·0091
0·1006	99·49	1·0052
0·1069	99·59	1·0041
0·1140	100·10	0·9990
0·1223	100·20	0·9980
0·1429	100·80	0·9920
0·1624	101·20	0·9881
0·1693	101·70	0·9825
0·1783	100·20	0·9980
0·2030	101·00	0·9901
0·2092	100·90	0·9911

continued on following page

TABLE III.- CONTINUED.

Wt.-% K	Resistivity of Amalgam $\times 10^{-6}$	Specific Conductivity of Amalgam $\times 10^{4}$
0·2113	101·40	0·9862
0·2156	101·60	0·9843
0·2271	102·00	0·9804
0·2462	102·77	0·9730
0·2659	103·57	0·9655

Resistivity of mercury = $96{\cdot}60 \times 10^{-6}$
Conductivity of mercury = $1{\cdot}0342 \times 10^{4}$

By plotting the electrical conductivity against the percentage of potassium in the alloy, two discontinuities are observed at 0·09% and 0·17% K.

The resistance of potassium amalgams of varying concentrations at different temperatures is given in Table IV.

TABLE IV.- ELECTRICAL RESISTANCE OF POTASSIUM AMALGAMS AT VARIOUS TEMPERATURES

Wt.-% K	Temp. °C.	Resistivity $\times 10^{-6}$	Specific Conductivity $\times 10^{4}$	Average Temperature Coefficient
0·0195	17·85	96·51	1·0862	
	21	96·79	1·0332	
	23	96·97	1·0314	0·00075
	27·20	97·22	1·0286	
	30·0	97·40	1·0266	
	32·0	97·51	1·0256	
0·1531	20·55	99·73	1·0027	
	22·45	100·01	0·9999	
	24·50	100·42	0·9959	
	27·10	100·69	0·9931	0·0010
	29·15	100·98	0·9903	
	31·00	101·18	0·9883	
	32·70	101·39	0·9863	
0·1582	22·62	100·36	0·9964	
	24·95	100·80	0·9920	
	27·20	101·01	0·9900	0·0010
	28·45	101·11	0·9890	
	29·95	101·21	0·9880	
	31·90	101·36	0·9866	
0·1891	18·85	99·10	1·0090	
	21·75	99·50	1·0050	
	24·25	99·70	1·0020	0·0010
	26·58	100·08	0·9992	
	30·00	100·40	0·9969	
	34·00	100·68	0·9932	
0·5591	17·95	101·40	0·9862	
	21·00	104·30	0·9588	
	22·90	105·00	0·9524	0·005
	25·35	106·80	0·9363	
	27·00	107·50	0·9302	
	29·40	108·60	0·9208	

The resistance of the amalgam increases as the temperature is raised, indicating that the conduction in amalgams is probably metallic and not electrolytic.

The temperature coefficients of alloys differ very little from 0·004, the normal value for pure metals, but they have a much lower value for solid solutions. In nearly all cases the temperature coefficients for potassium amalgams are less than 0·004 which would indicate that potassium amalgams behave like a solid solution of potassium in mercury.

Also, the conductivities calculated from the mixture law are higher than the observed values; potassium amalgams are therefore not merely mechanical mixtures of potassium and mercury, but behave like solid solutions.

Potassium amalgams heated initially to 100°C. show an increasing negative charge over the interval 68°–35°C. When the experiment is repeated with the same amalgam after standing for 10–20hr. it exhibits positive triboelectric phenomena at 50–52°C.[59] Dilute potassium amalgams which have a negative charge at room temperature retain this charge when they are solidified and again fused. Solid amalgams become negatively charged by rubbing with filter paper.[60]

Viscosity measurements of potassium amalgams have been made by several workers.[61–64] Degenkolbe and Sauerwald[62] and Roder and Morawietz[64] give the values shown in Table V.

TABLE V.- VISCOSITY OF POTASSIUM AMALGAMS

Wt.-% K	At.-% K	Viscosity (centipoises)		
		300°C.[62]	360°C.[62]	300°C.[64]
0	0	0·950	0·91	0·95
2·51	11·7	1·87	1·54	1·90
3·12	14·2	2·11	1·74	2·07
5·64	23·5	2·58	2·03	2·57
7·15	28·3	2·66	2·08	2·73
8·71	32·9	2·39	1·87	2·83
10·5	37·5	2·24	1·81	2·86
18·3	53·5	1·30	–	1·30
20·5	57·0	1·20	–	1·13
31·2	70·0	0·71	–	0·67
100·0	100·0	0·267	–	0·263

The isotherms of viscosity (280°, 300°, 320°C.) show a maximum near the composition of Hg_2K.[64]

The temperature dependence of viscosity is represented within 0·1% by $\eta = \eta_0$ exp. q/RT with η_0 independent of temperature. For pure mercury q = 657·9g.-cal.; for potassium amalgam of 0·191 at.-% K, q = 714·6g.-cal.[63]

Solid potassium amalgams float on the "mother liquor". The limiting value is 2·31% of potassium. Oily or pasty liquid amalgams are due to the presence of fine crystals in the liquid.[65] The values given in Table VI have been obtained for the densities of amalgams containing 0–0·182% of potassium at 30°C.[66] Determinations were carried out in benzene using a specific gravity bottle and the densities of the amalgams with respect to water calculated from the density of benzene.

The thermal expansion coefficient of potassium amalgams increases linearly with concentration; the specific volume increases linearly with concentration. The deduced atomic volume of potassium is 30% less than in the pure metal and the contraction decreases with increasing temperature.[61]

TABLE VI.- DENSITIES OF POTASSIUM AMALGAMS AT 30°C.

Wt.-% K	Density
0	13·52
0·056	13·47
0·068	13·46
0·101	13·43
0·126	13·41
0·156	13·39
0·171	13·37
0·182	13·36

The values given in Table VII have been obtained by Röder and Morawietz for the densities of liquid potassium amalgams at 320°C.[64]

The volume contraction is greatest near the composition HgK.

TABLE VII.- DENSITY OF POTASSIUM AMALGAMS AT 320°C.

K at.-%	Density g./c.c.	Additive at. Volume c.c./g.-at.	Measured at. Volume c.c./g.-at.	Contraction ΔV c.c./g.-at.
0	12·86	15·60	15·60	0
8·5	11·30	18·59	16·54	2·05
20·4	9·35	22·77	17·93	4·84
24·2	8·67	24·11	18·63	5·48
32·2	7·33	26·93	20·27	6·66
41·2	6·03	30·09	22·23	7·86
49·5	4·85	33·06	24·85	8·21
62·0	3·38	37·41	29·73	7·68
72·2	2·42	41·00	34·71	6·29
100	0·77	50·77	50·77	0

The surface tension of liquid potassium amalgams at the benzene interface has been measured and two discontinuities have been found in the interfacial tension/concentration curves indicating the formation of complexes of potassium with mercury.[66] The results are given in Table VIII.

TABLE VIII.- INTERFACIAL TENSION OF POTASSIUM AMALGAM AT 30°C.

Wt.-% K	Interfacial Tension dynes/cm.
0·000	100
0·056	86
0·068	83
0·101	88
0·126	87
0·156	86
0·171	94
0·182	91

For dilute potassium amalgams the following relationship holds: $d\sigma/d(\log a_2) = k$, where σ is the surface tension and a_2 the activity of potassium. Values of the surface excess are in agreement with the formation of a compound containing rather less than 6 atoms of mercury to 1 of potassium.[67] The surface tension of potassium amalgams prepared by the distillation of potassium vapour into mercury has been measured by Semenchenko *et al.*[68,69] and values are given in Table IX.

TABLE IX.- SURFACE TENSION OF POTASSIUM AMALGAM

Concentration	Surface Tension dynes/cm.	Reference
0·000	410	68
0·0024 at.-%	392	68
0·0080 at.-%	326	68
0·0183 at.-%	296	68
0·264 at.-%	284	68
0·00164 g.atom/l.	392	69
0·00289 g.atom/l.	368	69
0·00540 g.atom/l.	326	69
0·0123 g.atom/l.	296	69
0·0252 g.atom/l.	289	69
0·0257 g.atom/l.	286	69
0·0830 g.atom/l.	282	69
0·0918 g.atom/l.	283	69
0·1782 g.atom/l.	284	69

The surface tension first decreases with increasing concentration of the metal and then is almost constant. Pugachevich and Timofeevicheva[70] have found that a potassium content of 5×10^{-5} wt.-% at 20°C. produces a sharp fall in surface tension from 470 to 415 dynes/cm. but that further increases in potassium content cause a much slower decrease in surface tension. Between 0·1 and 0·6 at.-% of potassium, the surface tension falls linearly from 390 to 375 dynes/cm. Measurements have also been made between 20° and 350°C. to determine the effect of temperature. Up to about 0·6 wt.-% of potassium, the fall of surface tension with increasing temperature is non-linear, the curve being slightly concave to the temperature axis. Like sodium, potassium is surface active but more so; the maximum adsorption at 20°C. is 2·3 times as great for potassium as for sodium and the concentration corresponding to maximum adsorption with sodium is 3·5 times that of potassium. The limiting surface activity falls with rising temperature.[71]

Dilute potassium amalgams react with water in the dark at a rate which can be measured by the volume of hydrogen generated. Exposure to light from a carbon arc, $\lambda = 3660-5250$ A., accelerates the reaction but the light intensity was not measured nor its constancy discussed. Whereas sodium amalgams react in such a way that there is a steady increase in the initial rate with concentration of sodium in the light over the dark reaction, the difference between the rates approaching something like constancy after the first 30 min., no such regularity is found with potassium amalgams containing 0·038, 0·041, 0·056 and 0·101 wt.-% K during the first hour for which the experiments are reported.[72]

The influence of polarized light on the reaction of potassium amalgam with water has been examined by Anand and Bhatnagar[73] and, as for the reaction of sodium amalgam with water, the results show that the influence of polarized light is selective, being most effective when the electric vector vibration is parallel to the incident plane and least effective when perpendicular to the incident plane.

The decomposition of potassium amalgam in a dilute alkaline solution (0·01–0·4N. KOH) has been studied by Kapstan and Iofa;[74] Kt, where K is the rate constant and t the time, is shown to be a linear function of $C^{1/2}$, where C is the variable metal concentration in the amalgam. This relation is not valid at the start of the reaction because the solution is stirred by the introduction of the amalgam, nor at its end because the surface of the amalgam becomes contaminated. The rate of the reaction is determined by measuring the volume of hydrogen evolved. The activity of potassium is proportional to its concentration. The potential of the amalgam against the hydrogen electrode in the same solution has also been determined; this overvoltage η is $1{\cdot}507-0{\cdot}105 \log C_1 + 0{\cdot}118 \log i$, where C_1 is the OH^- concentration and i the current strength in amps., as measured by the rate of hydrogen evolution. This agrees with the theory predicting that the coefficients of $\log C_1$ and $\log i$ will both be equal to $2RT/F$. The overvoltage is lowered and the rate of reaction increased when the compound $(Bu_4N)_2SO_4$ is present in solution.

Fraenkel and Heinz[75] have determined the rate of reaction and the potential of a potassium amalgam, containing 0·46% K and prepared by the electrolysis of potassium chloride solution using a mercury cathode, when treated with 0·1 N.-hydrochloric acid in the presence of potassium chloride. The rate of reaction is determined by measuring the volume of hydrogen evolved. The same type of curve, Fig. 6, is obtained as for sodium amalgam. There is no induction period; the reaction proceeds at a constant initial rate of 9·5 ml. H_2/min. until just before the end when the rate falls practically to zero as the last traces of metal dissolve. The potential of the amalgam remains steady at about −2·18 volts (measured against a standard calomel electrode) until the rate of gas evolution decreases and then drops suddenly and then more gradually until finally it reaches the null point.

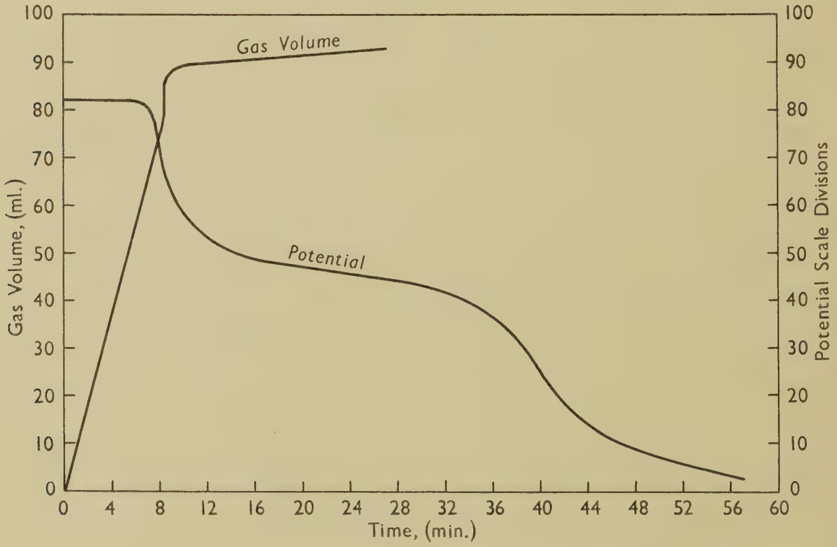

FIG. 6. RATE OF REACTION OF K/Hg WITH 0·1 N. HYDROCHLORIC ACID

Moriguchi and Sato[76] find that the reaction velocity between potassium amalgam and dilute sulphuric acid is almost independent of the initial concentration of the amalgam, and at constant temperature is proportional to the concentration of the acid. The increase of reaction velocity with temperature is smaller than that for a homogeneous system.

As may be seen from Fig. 7, liquid potassium and liquid aluminium are practically insoluble in each other at the m.p. of aluminium. The addition of potassium to aluminium, or of aluminium to potassium, does not affect the melting point of the pure elements.[7, 21]

The phase diagram for the system potassium–thallium is shown in Fig. 8.[7]

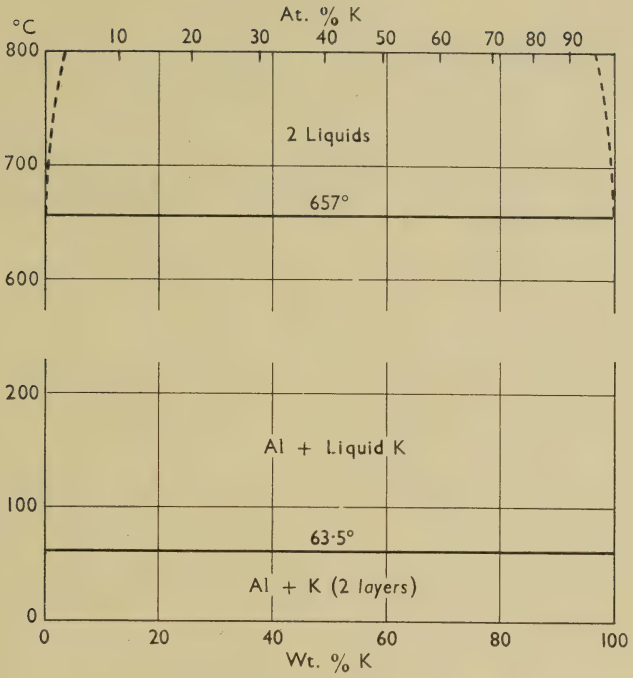

FIG. 7. THE SYSTEM Al–K

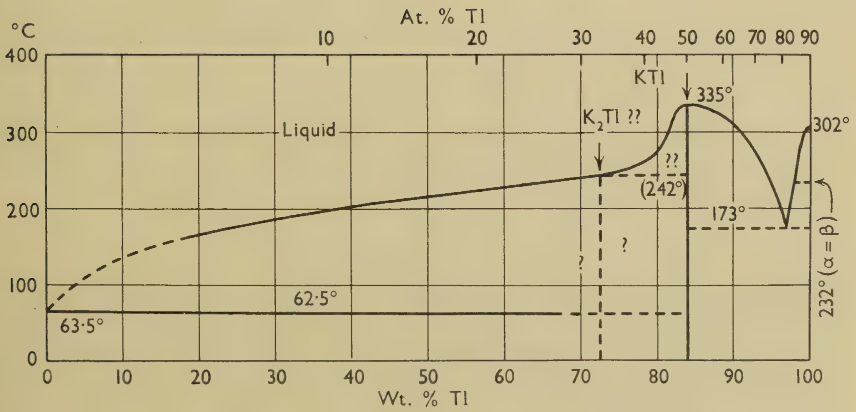

FIG. 8. THE SYSTEM K–Tl

There is some doubt as to the composition of the compound shown as K_2Tl, and its existence has not been confirmed by e.m.f. measurements for the cell $Tl/K^+/Tl_xK_{1-x}$.[21] The compound KTl has not the space-centred cubic crystal structure of the corresponding sodium compound, NaTl.[77]

The phase diagram for the potassium–tin system, Fig. 9,[7,21] has been prepared from thermal analyses. The liquidus temperature lies above the boiling point of potassium, and experimental difficulties are encountered in the region from 75–86% Sn. Four compounds are shown, K_2Sn, KSn, KSn_2 and KSn_4. The existence of these compounds is confirmed by e.m.f. measurements for the cell Sn/K^+ in pyridine/Sn_xK_{1-x}. Bergstrom[78] has observed the formation of a compound soluble in liquid ammonia to which the formula K_4Sn_8 has been assigned.

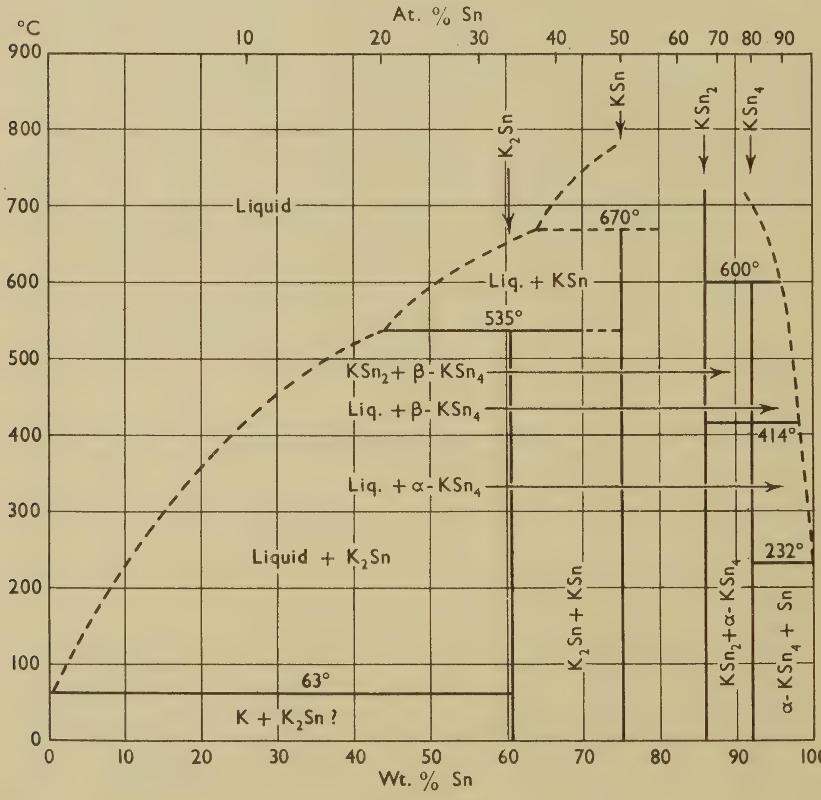

FIG. 9. THE SYSTEM K–Sn

The potassium–lead phase diagram is shown in Fig. 10.[7,21] There are four compounds shown, K_2Pb, KPb, KPb_2, KPb_4, but there appears to be some doubt about the actual phases which separate out. From their work on the hardness of lead-rich alloys with potassium, Tammann and Rüdiger[79] conclude that potassium is not markedly soluble in solid lead. Kremann and Pressfreund[80] have measured the e.m.f. of cells of the type Pb/K^+ in pyridine/Pb_xK_{1-x}. Points of inflexion occur on the e.m.f./concentration curve at 33 and 80at.-% Pb corresponding to the compounds K_2Pb and KPb_4. There is no evidence of the existence of KPb_2 or KPb shown as X in the phase diagram.

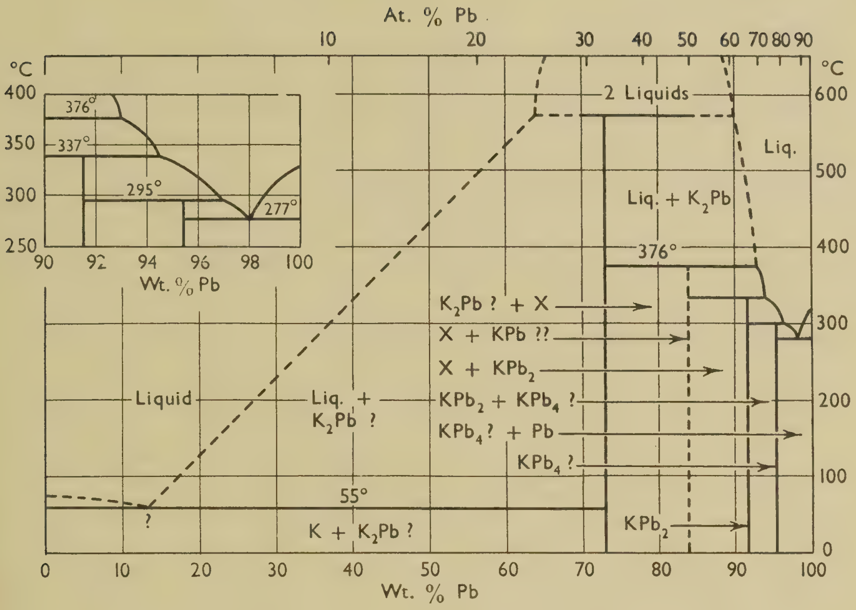

FIG. 10. THE SYSTEM K–Pb

The compound K_4Pb_9 has been found to be present as the only stable compound in liquid ammonia solution.[81]

The potassium–antimony system has been investigated by thermal analyses, the alloys being prepared by melting the elements together in a stream of hydrogen. The compounds K_3Sb, and KSb are shown in Fig. 11.[7,21]

The phase diagram for the potassium–bismuth system, Fig. 12[7,21] shows the presence of the compounds Bi_2K, Bi_2K_3, βBiK_3 and αBiK_3. There is some doubt about the composition Bi_7K_9. Two inflexion points are found on the e.m.f./concentration curve at 33 and 75at.-% K, corresponding to the compounds Bi_2K and BiK_3. The compound Bi_2K has a cubic lattice. (see also page 1580).

Potassium lowers the surface tension of bismuth. Pugachevich and Altynov[82] have measured the surface tension of pure bismuth and of bismuth–potassium alloys containing 0·00067, 0·0038, 0·0049, 0·0111, 0·0250at.-% K between 260° and 500°C. and find that potassium is more active than sodium at all temperatures. The maximum adsorption of potassium decreases with rising temperature. Altynov[83] has shown that the greater the surface tension lowering of bismuth by the addition of 0–0·5at.-% K, or the higher the surface activity of the mixture, the more the microhardness of the alloys increases. Alekseevskii[84] measured the electrical resistance, the magnetic moment and the critical magnetic field, Hc, of three samples of the compound Bi_2K using different preparations, and found that the compound becomes a superconductor at 3·57°K. The value of dHc/dT is approximately 160 gauss per degree. The high magnetic moment, the coincidence of the values of Hc for different samples, and the evolution of heat in its formation confirm the stable nature of the intermetallic compound. The compound Bi_2K_3 has a transition point at 3·6°K. but BiK_3 is not superconducting down to 1·4°K.[85]

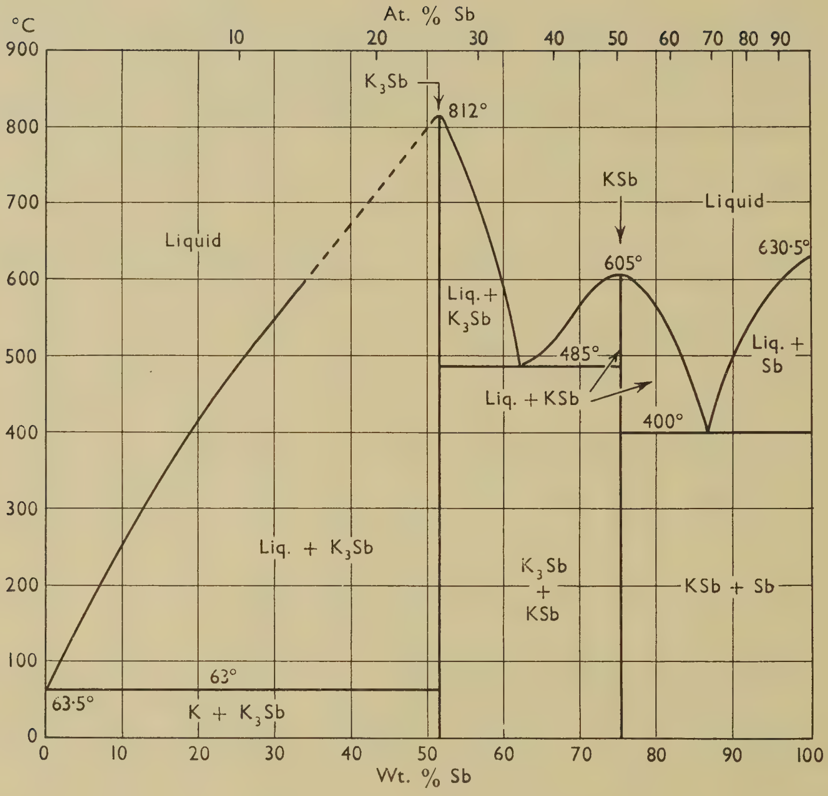

FIG. 11. THE SYSTEM K–Sb

The phase diagram for the potassium–sulphur system c.f. Fig. 13 shows the presence of K_2S, K_2S_2, K_2S_3, K_2S_4, K_2S_5, K_2S_6.[7,21,86-88] (See also pages 1564 and 1578).

Compounds of potassium and selenium have been described having the formulæ, K_2Se, K_2Se_3, K_2Se_4, but thermal analysis has not been carried out.[21] (See also page 1578).

The known compounds of potassium and tellurium are K_2Te and K_2Te_3.[21] (See also page 1579).

The simultaneous addition to cast iron of <0·015–0·02% (preferably 0·008%) of three of the elements, boron, potassium, sodium, lithium, calcium, magnesium, barium and cerium, is said to cause graphite to precipitate out in nodular form. The combined amount of the alloying ingredients should be <0·2–0·5%. The cast iron is claimed to be improved in that tensile strengths up to 78 kg./sq. mm. and elongations up to 3·5%, measured with test rods 50 mm. long, are obtained.[89]

Potassium may be used in place of lithium in the refining of zinc to

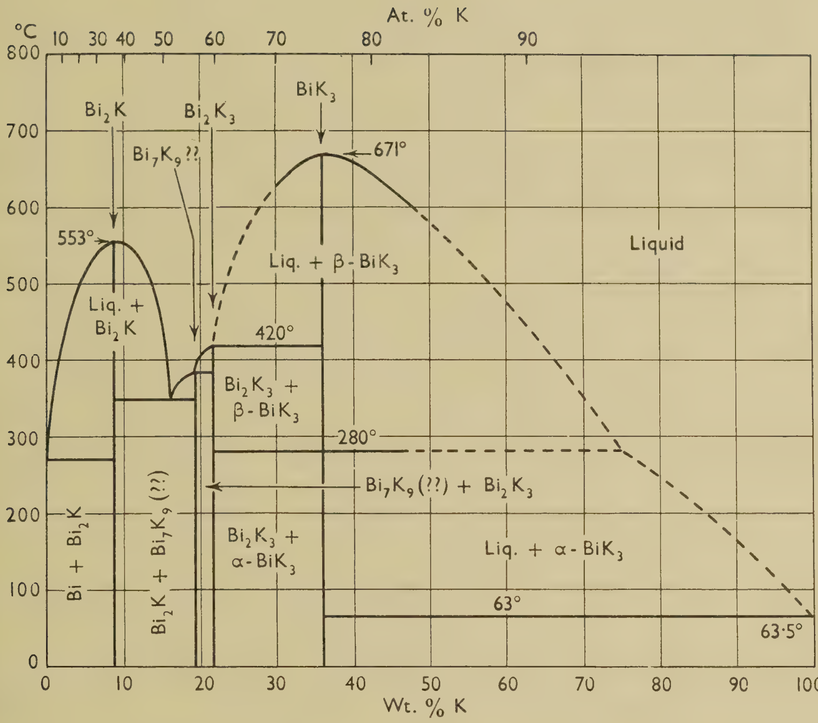

FIG. 12. THE SYSTEM Bi–K

remove impurities such as lead, tin and cadmium.[90]

A systematic study of the potassium–arsenic system does not appear to have been made. The only compounds described are KAs_2 and K_3As.[21]

Platinum is attacked by potassium vapour and a mass of black material is formed.[21]

The e.m.f. of cells of the type (Hg, alkali metal) liq./alkali hydroxide aq./(Hg, alkali metal, Tl) liq. has been measured by Wagner.[91] When the concentration of potassium is about 0·05at.-% and the molar fraction of thallium, N_{Tl}, is 0 to 0·8, dE/dN_{Tl} for the Hg–K–Tl system is 0·79 volts using dropping amalgam electrodes at 25°C.; $d\ln\gamma(K)/dN_{Tl}$ is 30·8.

Equilibria in systems rich in lead and containing alkali and alkaline earth metals have been studied by Jollivet.[92] For the system Pb–Bi–Mg–K, mixtures containing Bi, 0·03–0·5, Mg 0·04–0·38, K 0·01–0·20%, the rest lead, have been used. The points of one region (solid compound K_2MgBi_2) fit the equation:

$$2 \log (\mathrm{Bi}) + \log (\mathrm{Mg}) + 2 \log (\mathrm{K}) = -13{\cdot}26,$$

all concentrations being atomic concentrations of the liquid. The points correspond to a region of metastable equilibrium. The points of a second region (solid compound, $K_9Mg_6Bi_7$) fit the equation: $7 \log (\mathrm{Bi}) + 6 \log (\mathrm{Mg}) + 9 \log (\mathrm{K}) = -59{\cdot}54$.

Refs. p. 1616

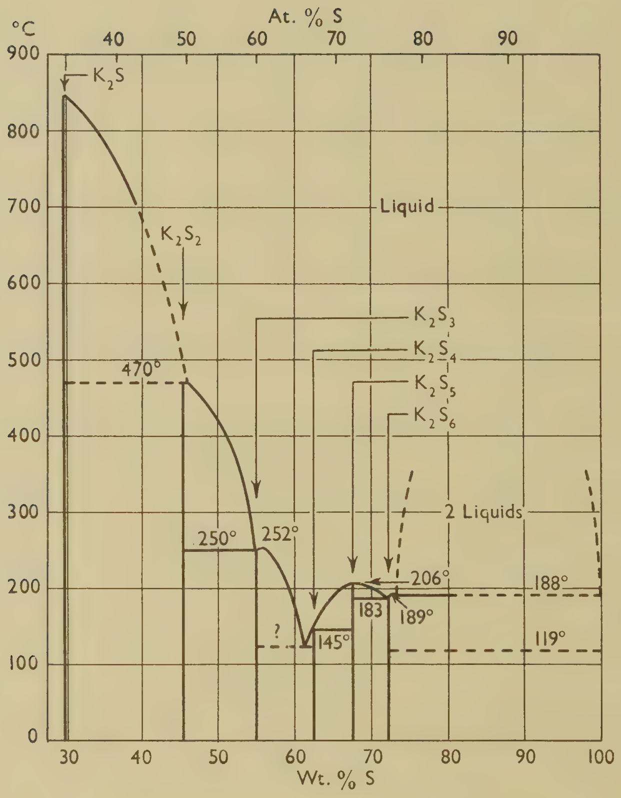

FIG. 13. THE SYSTEM K-S

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SECTION XLVII

POTASSIUM HYDRIDE

By A. R. BURKIN

Preparation and Thermal Dissociation

If potassium metal is heated in an atmosphere of pure hydrogen, potassium hydride is produced; the dissociation curves indicate that an equilibrium is reached.[1] The heat of dissociation was calculated as 13·34 kg.-cal./mole[2] from measurements of the dissociation pressure p obtained by enclosing potassium hydride in a nickel tube with walls 1·5 mm. thick. The tube was permeable to hydrogen below 390°C. but not above that temperature. The equilibrium was found to be perfectly reversible and the equation $\log p = (-5850/T) + 11{\cdot}2$ fitted the results, where T is the temperature and p is in mm. In later work,[3] extending the observations to sodium, rubidium and caesium hydrides, two methods were employed; direct observation of the appearance and disappearance of hydride on the metal surface on varying the temperature at a given hydrogen pressure, and using a nickel membrane. The metals react below the melting point and pure metal-free hydrides can be prepared using 3 atm. pressure of hydrogen at 50°C. The logarithm of the reaction velocity was found to be linearly dependent on temperature with a break in the line at the m.p. of the metal. At 100°C., 0·0105 c.c. of hydrogen combines per square cm. of potassium metal surface per hour. Although oxidation decreases the reaction rate, small quantities of oxygen do not alter the course of the reaction curves.

Alkali metal deuterides can, of course, be prepared in the same way as hydrides[4] and the former were reported to have slightly higher dissociation pressures than the latter.[5] Other measurements between 270°C. and 390°C.[6] gave calculated heats of formation of 14·15 and 14·45 kg.-cal./mole for potassium hydride and deuteride respectively. The difference was stated to be about equal to the probable experimental error. It was suggested that in view of the considerable difference in the dissociation pressures, hydrogen could be separated from deuterium by passing the mixed gases over heated potassium. A theoretical study of the factors influencing the equilibrium distribution of deuterium and hydrogen in hydrogen isotope exchange reactions led to the conclusion that a maximum redistribution coefficient occurs for the exchange of hydrides of the heaviest alkali metals with a non-metal hydride.[7]

Potassium hydride does not dissolve in potassium metal at temperatures up to 150°C.[3] but it is frequently convenient to produce the hydride in the presence of a diluent. The fused eutectic mixture of potassium chloride and lithium chloride, when dry, is a true solvent for sodium or potassium hydride[8] and it has been claimed[9] that if an alkali metal is heated with its halide above the m.p. of the latter but below the dissociation temperature of the metal hydride, in the presence of hydrogen, a solid solution of the hydride in the halide is formed. A somewhat similar method of preparation has been used employing the alkali chloride or carbonate as a diluent.[10]

Physical Properties

The heats of hydrolysis at infinite dilution and at 25°C., of potassium hydride and potassium metal according to the reactions

$$\text{KH (s)} + \text{H}_2\text{O (l)} \rightarrow \text{KOH} (\infty) + \text{H}_2\text{ (g)}$$

$$\text{K (s)} + \text{H}_2\text{O (l)} \rightarrow \text{KOH} (\infty) + \tfrac{1}{2}\text{H}_2\text{ (g)}$$

are −31·89 ± 0·12 and −47·05 ± 0·10 kg.-cal./mole respectively, giving the heat of formation of the hydride as −15·16 ± 0·16 kg.-cal./mole.[11] Results were obtained also for lithium and sodium hydrides.

The density of potassium hydride has been determined pycnometrically as 1·47.[12] Numerous estimates of the lattice energies and binding energies of the alkali metal hydrides have been made. Using the value of 17 ± 1 kg.-cal. for the electron affinity of the H^- ion the lattice energy of potassium hydride was calculated to be 166 kg.-cal./mole.[13] The equilibrium distance for the potassium hydride molecule was calculated as 2·1 A.[14] but the binding energy, calculated also, was too low, the error being attributed to failure to allow for the inter-electron effects. The binding energy has also been calculated using a value of $1{\cdot}80 \times 10^{-24}$ c.c. for the polarisability of the H^- ion[15] but it has been pointed out[16] that values of 9·0, 10·2 and $14{\cdot}6 \times 10^{-24}$ c.c. have previously been obtained for this ion. Use of these figures in the equations leads to a negative dipole moment for the hydride. The force constants and bond orders of a number of volatile hydrides and gaseous alkali hydrides have been estimated[17] and used to interpret some properties of the hydrides.

The emission spectrum of potassium hydride, obtained by using an arc in a hydrogen atmosphere, has been studied.[18-20] The coincidences between the lines of the hydride and lines in the solar spectrum are numerically equal to those to be expected by chance and it is concluded that potassium hydride is not present in the sun.[21]

Potassium hydride can be used in photoelectric cells and details of the preparation of these have been given.[22] The constancy of emission of gas-filled potassium hydride (and cæsium hydride) cells, after a glow discharge had been passed momentarily, has been determined at several anode voltages[23] and it was concluded that measurements should be made immediately after the discharge, which should be of very short duration. Photoelectric emission by potassium hydride begins in less than 3×10^{-9} sec. after the beginning of illumination of the hydride surface.[24]

Potassium bromide is sensitised to light if small amounts of potassium hydride are present in solid solution and such a system has been treated as a model in a study of photoelectric phenomena.[25] The photochemical decomposition of the hydride in the bromide, studied by observing the absorption of light of wave-length 2800 A., proceeds with a quantum efficiency of 0·27 at room temperature and nearly 1 at 500°C.[26,27] With light of wave-length 2265 A. the quantum efficiency is given as about 0·4 from −250 to −175°C., decreasing to a minimum of less than 0·1 at −75° and rising to about 0·2 at room temperature.[28] Below −100°C. the reaction products are not *F*-centres but intermediate products. The temperature coefficient of the decomposition rate differs if potassium deuteride is used instead of the hydride since the mechanism of the photochemical reaction consists of ejection of an electron from the *U* centre and diffusion away of the hydrogen or deuterium.[29]

Irradiation with γ-rays causes colour changes in potassium bromide crystals sensitised with the hydride. These are so pronounced that the unaided eye can detect the change corresponding to a dose of 50 roentgen.[30] At −180°C. the photochemical action of *X*-rays on the sensitised potassium bromide crystals gives colour centres as the reaction product. The energy, *E*, required for stabilisation of a colour centre depends linearly on the ratio of the density of the total energy absorbed by the crystal, *W*, and the initial hydride concentration u_0. The relationship is given as

$$E = E_0 + \epsilon W/u_0$$

where the constant $\epsilon = 4{\cdot}6$ and the initial energy requirement $E_0 = 35$ e.V.[31] The curve relating the concentration of colour centres, F, to the potassium hydride concentration, u, is represented by $F/u = 1/\epsilon \log(1 + \epsilon W/E_0 u)$.[32] In this paper E_0 is given as 41 e.V. and $\epsilon = 4{\cdot}4$. With potassium chloride similar results were found: $E_0 = 26$ e.V. and $\epsilon = 6{\cdot}7$. The value of E_0 remains constant between 20°C. and 160°C. A temperature rise leads to more rapid saturation of the reaction and the value of ϵ, a kinetic constant, for potassium bromide increased from 4·4 at 20°C. to 7·6 at 100°C. and to 15 at 160°C.

The quantum yield for the photochemical decomposition on irradiation with X-rays decreases from unity at 500°C. to 0·05 at −80°C.[33] The value of about 0·24 was obtained for the production of colour centres at room temperature.[34] Studies of the absorption spectra of pure potassium bromide crystals and those sensitised by potassium hydride indicate that the colour centres produced by exposure of the latter to X-rays at temperatures around −183°C. are stable on warming, the stabilisation consisting in the localisation of defect electrons.[35]

Chemical Properties

Few reactions of potassium hydride have been reported, presumably because other metal hydrides are more convenient as reducing agents. Boron hydrides can be prepared from boron halides, the hydride of a metal including potassium, and hydrogen.[36] The salt, KBH_4, cannot, however, be prepared by reaction of potassium hydride with diborane between −185°C. and 200°C. with diborane pressures between 170 and 700 mm. of mercury. Between 180°C. and 200°C. the diborane polymerises.[37] However, the reaction between $KB(OCH_3)_4$ and diborane does give potassium borohydride.[38]

Industrial Uses

The production of strongly reducing conditions at a slag-metal interface by the dissociation of some metal hydrides into nascent hydrogen and alkali metal has been used to reduce the sulphur content of molten ferrous metals to as little as 0·009%.[39] Only about 0·5% of the alkali metal hydride is required and the action of additions for other purposes, e.g. stabilisation of carbides, is not inhibited.

Alkali metal hydrides, ground finely in a ball mill in the presence of xylene or hexane, catalyse ester-ester exchange when present at about 0·05 to 0·5% of the mixture at 0–120°C. in the absence of water. A number of such interchanges are reported[40] including the molecular rearrangement of completely esterified esters of glycerol and a mixture of fatty acids such as a vegetable or animal oil and the exchange between aromatic carboxylic acid esters of a monohydric alcohol, e.g. dimethyl phthalate, and aliphatic carboxylic acid esters of a polyhydric alcohol, e.g. triacetin.

Alkali metal hydrides also catalyse polymerisation reactions under some conditions. Thus anhydrous ϵ-caprolactam when mixed with 0·3 − 0·5 mole % of a hydride and heated to about 250°C. in an atmosphere of nitrogen gives a polymer within a few minutes. This has a high melting point and can be formed into oriented fibres or films.[41] Also carbon monoxide treated with a mono-olefin such as ethylene at a temperature of about 250°C. under pressure (1000 atm.,) in the presence of one of a series of catalysts, including alkali metal hydrides, in water and toluene gives an ethylene-carbon monoxide polymer with a molecular weight of about 500. If ammonia or an amine is present in the reaction mixture this also appears in the polymer.[42]

The alkali metal hydrides also cause fats to recrystallise in a different form, lard producing a material resembling vegetable fats in some respects.[43]

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SECTION XLVIII

THE OXIDES OF POTASSIUM

By D. M. MCC. STEELE

The oxides of potassium mentioned in the literature are:- K_2O, potassium monoxide, K_2O_2, potassium peroxide, (K_2O_3), potassium trioxide, $KO_2(K_2O_4)$, potassium superoxide, (KO_3, potassium ozonide).

There appears to be some doubt as to the sufficient characterisation of the trioxide, K_2O_3.

The oxide now called the superoxide, KO_2, was for some time thought to be the dimer, K_2O_4. Magnetic measurements, *X*-ray data and colour, however, suggest the monomeric formula, KO_2. This is the most stable of the oxides.

The monoxide and trioxide have been less well characterised than the peroxide and superoxide.

POTASSIUM MONOXIDE

Potassium monoxide, K_2O, is formed by reduction of the higher oxides. Such reduction occurs, for example, during the preparation of potassium peroxide by oxidation of potassium metal in liquid ammonia by means of oxygen,[1] unless the temperature is kept below −50° C.

The monoxide is one of the final products in the thermal decomposition of potassium cyanate, KNCO. The decomposition involves the KO radical and is considered to proceed as follows: in the equilibrium between KOCN and KNCO, the latter dissociates into K^+ and NCO^-; then:-

$$2NCO^- \xrightarrow{\text{rapidly}} N_2 + 2CO$$

$$CO + KNCO \overset{\text{rapid at } 600^\circ C.}{\rightleftharpoons} KCN + CO_2$$

$$\text{then } K^+ + CO_2 \rightarrow KO^\bullet + CO$$

$$\text{and } K^+ + KNCO \rightarrow KCN + KO^\bullet$$

$$\text{finally } KO^\bullet + KOCN \rightarrow K_2O + NCO^-$$

The NCO^- ion then decomposes again as above. The kinetics of this decomposition have been studied[2] and the rate determining step is the dissociation, $KNCO \rightleftharpoons K^+ + NCO^-$.

The monoxide can be prepared in the laboratory by interaction of the nitrate and the metal:

$$10K + 2KNO_3 \rightarrow 6K_2O + N_2$$

On an industrial scale the monoxide may be produced by calcining natural calcium phosphate with a silicon-aluminium-potassium mineral, phosphorus pentoxide being also liberated in the reaction[3].

Physical Properties

Potassium monoxide is a white solid, yellow when hot, which sublimes at 881°C. under a pressure of 600 mm. of mercury.[4]

The crystal has the fluorite (CaF_2) structure with a lattice constant of 6·436[5]. The atomic refraction of potassium in the monoxide has been derived and found to be 2·75[6].

The heat of formation of potassium monoxide is 86·2 kg.-cal.

The molecular volume is 17·7.[7] The contraction constant, defined by the molecular volume of the compound divided by the sum of atomic volumes of constituent elements,

$$\text{i.e.,} \frac{V_m}{\Sigma V_a} = C; \ m \text{ is } 0{\cdot}40 \text{ for potassium monoxide.}$$

From this it is deduced that since $C < 1$, the monoxide is a conductor in the fused state and, further, that as $C < 0{\cdot}65$. it is a typically ionic compound.[8]

Chemical Properties

Potassium monoxide reacts with water to give potassium hydroxide without liberation of oxygen:-

$$K_2O + H_2O \rightarrow 2KOH.$$

In liquid ammonia it ammonolyses to give potassium hydroxide and amide.[9]

$$K_2O + NH_3 \rightarrow KOH + KNH,$$

This reaction precludes the preparation of the monoxide by oxidising potassium in liquid ammonia.

Systems of oxides containing the monoxide are numerous and some are important, particularly $K_2O–Al_2O_3–SiO_2$, but generally the presence of potassium monoxide is of secondary importance and such systems are discussed under the characteristic element present.

Uses

The uses of potassium monoxide fall under two main headings, ceramics and catalysis.

The monoxide of potassium is an important constituent of many ceramic materials, particularly in the $K_2O–SiO_2–Al_2O_3$ system: most of the applications in this field will be discussed in later supplements devoted to the chemistry of silicon and aluminium. The importance of the presence of the monoxide in aluminomagnesia glass has been indicated by Tukh and Tugusheva.[10] An increase in the amount of potassium monoxide at the expense of sodium monoxide (keeping R_2O constant) makes melting and subsequent treatment easier: the properties of the glass are also much improved.

The second important use of the monoxide is as an activator or promoter in catalysis, particularly in organic chemistry. It is used as an activator in the catalytic synthesis of ammonia,[11–26] and in the Fischer-Tropsch process.[27–34] The presence of potassium monoxide in vanadium pentoxide increases the catalytic oxidation of sulphur dioxide to the trioxide.[35,36]

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DIPOTASSIUM DIOXIDE (POTASSIUM PEROXIDE)

Potassium peroxide, K_2O_2, has been prepared by passing oxygen through a solution of potassium in liquid ammonia at a temperature between −50 and −60°C until the colour of the free metal disappeared.[1] The apparatus used, as described by Kraus and Whyte,[2] provides a means for measuring oxygen absorbed in the oxidation process or evolved when the oxide is treated with water. The samples of potassium used were filled into weighed, fragile glass bulbs and introduced into a weighed reaction tube. The weight of the product formed upon oxidation is not a satisfactory criterion of purity of potassium peroxide because of the formation of some monoxide which ammonolyses[3] to potassium hydroxide and potassium amide, KNH_2, the latter compound being readily oxidised.

The use of lower temperatures is not practicable because the colloidal solution of the peroxide becomes extremely viscous while, at higher temperatures, measurable quantities of the peroxide are reduced to the monoxide which, in turn, ammonolyses.

In order to determine the nature of the reaction product, it was treated with water. Potassium peroxide dissolves in ice-cold water without the evolution of oxygen. At higher temperatures oxygen is evolved:-

$$K_2O_2aq \rightarrow KOHaq + \tfrac{1}{2}O_2$$

Refs. p. 1627

Physical Properties

Potassium peroxide is an orange coloured solid. When prepared in liquid ammonia, its colour is cream or white, owing to strong adsorption of ammonia. When the atmosphere of ammonia is removed at room temperature or below, the colour becomes bright yellow and this colour change is reversible. When all the ammonia is removed by prolonged heating in vacuo at 100°C. the oxide becomes olive-brown.[1]

The peroxide melts at 490°C. and dissociates under 1 atm. pressure at 779°C. The heat of formation is 118·5 kg.-cal. The dissociation pressure, p, at given temperature T° is given by the equation:-

$$\log p = [(-A/4{\cdot}571T) + 1{\cdot}75 \log T - (BT/4{\cdot}571) + 2{\cdot}8]$$

The values for the constants A and B for potassium peroxide are: $A = 53{,}000$ and $B = 0{\cdot}0190$. The heat of dissociation is +53·0 kg.-cal.[4,5] For the peroxide, $d_4^{25} = 2{\cdot}180 \pm 0{\cdot}001$[6]

Chemical Properties

Potassium peroxide reacts violently with oxygen at pressures as low as 1 cm.[1] At lower pressures, it is suggested, the trioxide, K_2O_3, is formed as an intermediate. The final product is the superoxide which cannot be oxidised further.

Ammonia is absorbed strongly by this oxide and is given off only with difficulty even at 100°C.

The peroxide absorbs water vapour, without the evolution of oxygen, to form a monohydrate, which is light pink in colour, and a dihydrate, which is white when free from ammonia. The dihydrate, in the presence of excess water vapour, loses approximately one atom of oxygen per molecule of water added:-

$$K_2O_2,2H_2O + H_2O \rightarrow K_2O,3H_2O + \tfrac{1}{2}O_2$$

The hydrates rearrange slowly at ordinary temperatures in the dry state with the formation of hydrated potassium monoxide, potassium superoxide and potassium hydroxide:-[1]

$$3(K_2O_2,H_2O) \rightarrow 2KO_2 + 4KOH + H_2O$$
$$3(K_2O_2,2H_2O) \rightarrow 2KO_2 + 2(K_2O,3H_2O)$$

The decomposition of the peroxyhydrate:-[7]

$$3(K_2O_2,2H_2O_2) \rightarrow 2KO_2 + 4(KOH,H_2O) + 3O_2$$

has been investigated with the aid of magnetic measurements which give the amount of the yellow paramagnetic KO_2 formed at the expense of the diamagnetic K_2O_2. Kazarnovskii and Neiding[7] prepared the peroxyhydrate, K_2O_2, $2H_2O_2$, by evaporating at room temperature over concentrated sulphuric acid solutions containing two moles of hydrogen peroxide to one mole of potassium hydroxide. The compound is quite stable at the temperature of solid carbon dioxide. In the spontaneous decomposition at 0°C., the molar ratio of superoxide formed to oxygen evolved remains approximately constant and coresponds to a conversion ranging from 1% to about 50%: this is evidence for the absence of chain reactions. Beyond that point, the amount of superoxide formed falls increasingly below the amount of oxygen evolved. If the water formed in the reaction is eliminated, the conversion from peroxide to superoxide can be raised to 91%. This proves that the main reaction is an oxidation of the peroxide to superoxide by hydrogen peroxide:-

$$K_2O_2,2H_2O_2 \rightarrow 2KO_2 + 2H_2O$$

Refs. p. 1627

The secondary reaction is the decomposition of superoxide by water:-

$$2KO_2 + 3H_2O \rightarrow 2[KOH,H_2O] + 1\tfrac{1}{2}O_2$$

The main reaction is taken to occur through passage of an electron from the $O_2^{=}$ ion to hydrogen peroxide with rupture of the O-O bond and formation of a free OH radical:-

$$K_2^{++}O_2^{-}\ (H_2O_2)_2 \rightarrow K^+O_2^- + K^+OH^- + H_2O_2 + OH$$

The OH radical then reacts with hydrogen peroxide to give HO_2. This mechanism accounts for 50% of the conversion as opposed to the 90% observed. To account for this additional conversion, a second mechanism is postulated involving the reaction:-

$$KOH + HO_2 \rightleftharpoons KO_2 + H_2O$$

For this reaction: $\Delta H_{298} = -16 \pm 10$kg.-cal., $\Delta S_{298} = 1$g.-cal.deg.$^{-1}$, $\Delta F_{298} = -16 \pm 10$kg.-cal., and hence the equilibrium constant:-

$$p_{H_2O}/P_{H_2O} \approx 10^{12}$$

Consequently, under conditions where $p_{H_2O} \sim 10^{-3}$ atm. and water is removed continuously, this reaction should go from left to right even at p_{H_2O} as small as 10^{-15} atm. If water is not removed, the reaction goes from right to left and results in the destruction of the superoxide. From these results it is possible to formulate the mode of decomposition of hydrogen peroxide in alkaline solutions.

The monohydrate of the peroxide, K_2O_2,H_2O, may be oxidised to the monohydrate of the trioxide at room temperature.[1]

Uses

Potassium peroxide is employed as a flux in cutting stainless steels and alloys of high chromium content.[6]

Analysis

A method for the determination of oxygen in potassium peroxide using chlorine dioxide has recently been described[8] which avoids the formation of hydrogen peroxide from potassium peroxide and so eliminates errors arising from this reaction.

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DIPOTASSIUM TRIOXIDE

As was earlier remarked, the existence of potassium trioxide, K_2O_3, as a definite individual chemical compound has not been completely proven. Kraus and Parmenter claim to have prepared the compound by allowing oxygen to react with potassium peroxide at room temperature at low pressures.[1] The light cream colour of the peroxide gradually darkens and becomes a chocolate brown, which fades finally and becomes light yellow as the trioxide is converted into the superoxide, KO_2. At room temperature oxidation is rapid and

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still proceeds rapidly even at −33°C. Since only the colour of the oxide was used by these workers as an indication of the completeness of oxidation, it was not possible to prepare a compound of absolute purity.

Doubt as to the existence of this oxide has been expressed by Raikhshtein and Kazarnovskii.[2,3] The dissociation points of the suspected oxide and of the products of its thermal disintegration up to K_2O_2 were measured. It was found that even the first measurements of the thermal disintegration kinetics at 360°C and 0·1mm. pressure suggested that K_2O_3 is not an individual compound but a mixture of KO_2 and K_2O_2. The curve is smooth and no discontinuity is found at the point corresponding to K_2O_3.

Physical Properties

Despite this uncertainty as to the existence of potassium trioxide, K_2O_3, some physical data have been published for such a compound. It is said to be chocolate brown in colour.[1] It melts at 430°C, and dissociates at 668°C; the heat of dissociation is +13·0kg.-cal. The heat of formation is 125·0kg.-cal. and the constants A and B in the dissociation pressure equation (see page 1626) are $A = 20{,}890$, $B = 0{\cdot}0168$.[4,5]

Chemical Properties

Potassium trioxide, K_2O_3, behaves like a mixture of K_2O_2 and KO_2. It is readily oxidised to the superoxide and reduced first to the peroxide and thence to the monoxide. One mole of the oxide absorbs one mole of water vapour at room temperature with the formation of a hydrate and without evolution of oxygen. During the reaction the brown colour of the oxide changes to the yellow of the monohydrate. If less than one mole of water is added per mole of the hydrated trioxide, the remainder of the oxide may be oxidised to the superoxide. The hydrate rearranges more slowly than either of the hydrates of potassium peroxide:-[1]

$$3(K_2O_3,H_2O) \rightarrow K_2O,3H_2O + 4KO_2$$

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POTASSIUM SUPEROXIDE

Potassium superoxide, KO_2, is formed by the oxidation of any of the aforementioned lower oxides of potassium. It is also formed in the spontaneous decomposition of the oxyhydrates and peroxyhydrates of potassium.[1] (see page 1626).

Several methods for the preparation of potassium superoxide in the laboratory have been described.

Kraus and Parmenter and Kraus and Whyte[2,3] oxidised potassium in liquid ammonia at −50°C. and obtained a product having a purity of 99%. The oxidation can be carried out at room temperature over a period of six weeks. Metallic potassium is dissolved in liquid ammonia which is then rapidly evaporated so as to spread the metal in a thin film over the surface of a tube of 300c.c. capacity. Oxygen is initially introduced at low pressure which is later allowed to rise to atmospheric pressure.

When a liquid amalgam of potassium in mercury is treated with oxygen, potassium superoxide is formed.[4] In thus giving the superoxide potassium differs from sodium and lithium which give the corresponding peroxides.

Extensive work on the structure of the superoxide has been carried out by Neuman,[5] and for these studies the potassium superoxide was prepared by the slow burning of potassium in incompletely dried oxygen at 300°C., since potassium burns only with great difficulty in very dry oxygen.

Physical Properties

It is now well established that the formula for potassium superoxide is KO_2 and not K_2O_4. The most convincing evidence in favour of the former structure is that obtained by magnetic measurements.[5-9]

If the formula is KO_2 the two possible structures for the O_2^- ion are:-

$$:\underset{\cdot\cdot}{\dot{\mathrm{O}}}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:^{-} \quad \text{and} \quad :\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\underset{\cdot\cdot}{\dot{\mathrm{O}}}:^{-}$$

These have the same energy and the actual structure is a resonance form which gives a $^2\Pi$ state containing a 3-electron bond, i.e.

$$:\underset{\cdot\cdot}{\dot{\mathrm{O}}}\overset{\cdot}{:}\underset{\cdot\cdot}{\dot{\mathrm{O}}}:$$

Since it contains an odd number of electrons such an ion would be paramagnetic and coloured: the superoxide of potassium is paramagnetic ($\mu = 2{\cdot}04$ Bohr magnetons).[5] On this evidence the formula assigned to this oxide is KO_2 and Neuman suggests the name, 'superoxide' instead of 'tetroxide.' Helms and Klemm suggest the name dioxide.[10]

The arrangement of potassium and oxide ions in the superoxide structure has been elucidated by *X*-ray analysis, Geometric evaluation of powder photographs according to the method of Debye-Scherrer with unfiltered CuKα radiation showed a hexagonal elementary cell with the dimensions $a = 5{\cdot}70$ A. and $c = 6{\cdot}72$ A. and including four molecules of KO_2. The structure is of the calcium carbide type, analogous to the structures of barium and strontium peroxides, BaO_2 and SrO_2, except that these lattices contain O_2^{--} ions while KO_2 contains the O_2^- ion. The space group is D_{4h}^{17}–$F4/mmm$. The co-ordinates of the four potassium atoms in the unit cell are: 0 0 0, 0 ½ ½, ½ ½ 0, ½ 0 ½, and those of the eight oxygen atoms are: ½ 0 0 $\pm u$, 0 ½ 0 $\pm u$, 0 0 ½ $\pm u$, ½ ½ ½ $\pm u$, where $u = 0{\cdot}095$. The lattice is formed by potassium ions which alternate with O_2^- ions. It is similar to a deformed potassium chloride lattice. The distance between the oxygen atoms of the ions of the molecule, $d_{\mathrm{O-O}} = 1{\cdot}28$ A.[10-14] The lattice energy for potassium superoxide has been calculated from the value c/a (= 1·178) by Ewald's method. It is found that the lattice energy,[15] V is 195·1 kg.-cal. mole.$^{-1}$

Potassium superoxide is a deep orange solid, m.p. 380°C. It dissociates at 660°C. under 1 atm. pressure and the heat of dissociation is +9·9 kg.-cal.[16] The heat of formation is 133·7 kg.-cal. The dissociation pressure p can be evaluated at any temperature T by using the equation already quoted (see page 1626); the values for the constants A and B in the equation are $A = 14{,}962$ and $B = 0{\cdot}0239$ for potassium superoxide.[17]

Warming and cooling curves for this oxide show a transition at −75·5±0·5°C This transition is associated with a change in colour on cooling from deep orange to light cream.[18]

Chemical Properties

Potassium superoxide reacts with water according to the equation:-

$$2KO_2 + 3H_2O \rightarrow K_2O,3H_2O + \tfrac{3}{2}O_2$$

one atom of oxygen being evolved per molecule of water added. Once breakdown of the superoxide has been initiated, it decomposes completely to potassium hydroxide while the remaining superoxide stays intact.

When water is added to potassium superoxide suspended in liquid ammonia there is no indication of reaction while liquid ammonia or ammonia vapour is present. On exhausting the tube at −30°C., about $^3/_5$ of the oxygen equivalent to the water added is evolved and the remainder is evolved as the product warms to 25°C.[2]

Attempts to form HO_2 by acidifying potassium superoxide at 0°C. have failed.[19]

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POTASSIUM OZONIDE

The nature of the reaction between ozonised oxygen and the alkali metal hydroxides has long been the subject of investigation. The resulting products of this reaction, which vary in colour from deep yellow to orange, were once thought to be derivatives of a hypothetical 'ozonic acid', H_2O_4, and hence were called 'ozonates'.

It has been observed[1,2,3] that potassium "ozonate" is soluble in liquid ammonia with the formation of a red solution; evaporation of the ammonia leaves a red solid which consists largely of a compound having the formula KO_3.

$$3KOH + 2O_3 \rightarrow 2KO_3 + KOH,H_2O + \tfrac{1}{2}O_2$$

The more logical and correct name for this compound now adopted is potassium ozonide.

Physical Properties

Potassium ozonide is a red solid.[1,2]

Refs. p. 1631

The *X*-ray powder diagram of a mixture of KO_3 (92·3%) and KOH (5·5%) shows that the size of the unit cell is $a = 6{\cdot}094$ A., $c = 7{\cdot}056$A. These data correspond almost exactly with the structure of potassium nitride, KN_3, the only significant difference between the photographs of the two compounds being the absence of the 121 line in the case of KO_3. This suggests that the O_3^- ion is not linear. On heating above 0° C., the lines of KO_3 disappear and those of KO_2 are observed.[4]

Chemical Properties

Potassium ozonide decomposes violently in water liberating energy in the form of light. It slowly decomposes at ordinary temperatures:-

$$2KO_3 \rightarrow 2KO_2 + O_2$$

Unlike sodium ozonide the potassium compound will liberate iodine from an acidified potassium iodide solution. This indicates that, in the case of potassium ozonide, KO_3 may not be the only species present. This is even more strongly suggested in the case of caesium ozonide, CsO_3.[1,2,3]

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SECTION XLIX

POTASSIUM HYDROXIDE

By L. PRATT

Many requirements for a strong alkali are met by sodium hydroxide (see Table I), but potassium hydroxide is preferred for some uses, e.g. as an electrolyte in cells and as an absorbent for carbon dioxide, since the potassium ion has a greater mobility than the sodium ion and some of its salts are more soluble than those of sodium.

Manufacture

Potassium hydroxide is usually manufactured by the electrolysis of aqueous solutions of potassium chloride in cells similar to those used in making sodium hydroxide (see page 649 and Mellor, Suppl. II, Pt. 1, p. 273 *et seq.*). The chloride solutions may be purified before electrolysis to remove substances which interfere with the process or which, like sodium, may contaminate the product. There are differences in the best conditions for the electrolysis of sodium and potassium chloride solutions[1,2] and in the detailed design of the cells, for those which work satisfactorily with sodium chloride may not work at all with the potassium salt.[3] Details have been given of mercury cells of German design which were used to make potassium hydroxide only.[4] In one type of diaphragm cell,[5] the anolyte solution (3% KCl) floats on top of the catholyte solution (26% KOH) from which it is separated by a thin layer of nitrobenzene, which is saturated with the potassium salt of dipicrylamine to allow it to conduct electricity.

TABLE I. - ANNUAL PRODUCTION OF SODIUM AND POTASSIUM HYDROXIDES IN THE U.S.A.[249]

	1956	1957
NaOH, electrolytic	3,794,963	3,975,609 tons
NaOH, lime soda	422,034	341,210
NaOH, total	4,216,997	4,316,819
NaOH, % electrolytic	90·0	92·1
KOH, 90% basis	92,342	83,898

Diaphragm cells give a solution containing 10–15% of potassium hydroxide, about 10% of potassium chloride and smaller amounts of carbonate, chlorate and other impurities, including sodium. Mercury cells give purer solutions containing about 30% of hydroxide with carbonate and sodium.

A solution of impure potassium carbonate can also be electrolyzed in a cell with a mercury cathode.[6] This gives an amalgam which is made the anode in a second cell and decomposed electrolytically to give a 30% hydroxide solution.

Potassium hydroxide solutions can be made in other ways, commonly by treating potassium salts with an hydroxide whose cation gives an insoluble salt with the anion of the potassium salt. The equilibrium $K_2CO_3 + Ca(OH)_2$

$\rightleftharpoons$ 2KOH + $CaCO_3$ has been studied.[7] The yield of potassium hydroxide is high in dilute solutions but decreases as the concentrations are increased, since a solid double carbonate $K_2CO_3,CaCO_3$ is formed. The potassium in feldspar ($KAlSi_3O_8$)[8,9] and in greensand[10,11] can be brought into solution as the hydroxide by heating the mineral with calcium hydroxide and water under pressure in an autoclave at about 300° C. for several hours.

Calcium hydroxide can also be used to make potash solutions from potassium oxalate,[12] potassium bicarbonate[13] or the borate K_2O,B_5O_8,[14] the oxalate and bicarbonate being made from potassium sulphate and the borate from potassium chloride.

A pure solution of the hydroxide about 20% more concentrated than those obtained directly by other methods is produced by treating potassium sulphate solution with barium hydroxide and filtering off the precipitate.[15] If a solution of barium hydroxide is passed through a cation exchange column containing potassium ions, those ions are displaced by barium ions and the eluate is a solution of potassium hydroxide.[16] The hydroxide solution may also be produced by treating a polybasic barium silicate with aqueous potassium sulphate at about 80° C.[17] Strontium hydroxide reacts with potassium sulphate[18] in the same way as barium hydroxide, and it is easier to convert the precipitated strontium sulphate to the hydroxide again. The equilibrium between potassium chloride and lead oxide has been studied.[19]

Potassium cyanide, made by heating potassium sulphate[20,21] or the double salt $MgCO_3,KHCO_3,4H_2O$[22,23] at about 1000°C. with carbon and nitrogen, is hydrolyzed by superheated steam to give potassium hydroxide and ammonia. Feldspars[24,25] and other potassium minerals such as leucite[26] give potash solutions when heated with calcium salts and leached with water. The production and composition of caustic potash suitable for soap manufacture have been reviewed.[27]

Concentration and Purification.

The solutions can be concentrated by evaporation in metal vessels and are sold commercially at 50% strength. The concentration is increased to 90% or more[28] by heating the solutions to 375° C. under reduced pressure in evaporators made of nickel, which is resistant to hot alkalies. Silver or gold or gold-plated apparatus[29] has also been used.

When cooled to about 20° C., solutions containing more than 61% of potassium hydroxide solidify and are cast into sticks or pellets.

Under atmospheric pressure, aqueous solutions of potassium hydroxide are not saturated at their boiling points and to remove the last few percent of water they must be heated to near the melting point of the hydroxide ($\sim$406°C.), either under reduced pressure or in an inert liquid of high boiling point.[30] The residual water may also be removed by the action of calcium carbide on droplets of the solutions suspended in a hot inert liquid.[31]

The solutions can be concentrated and purified by fractional freezing. In this way the dihydrate, $KOH,2H_2O$, is obtained almost free from sodium hydroxide and potassium chloride.[32] Potassium chloride, the main impurity in the solutions from diaphragm cells, crystallizes out during evaporation, but it can be separated by cooling the solutions until both the chloride and hydroxide (as dihydrate) crystallize.[33] The mixed solids are separated by flotation of the chloride in the mother liquor. Small amounts (0·75%) of the chloride can be removed by adding a surface-active compound (acetates of long chain aliphatic amines) to a concentrated hydroxide solution:[34] when the mixture is shaken, most of the chloride is carried away in the froth and only about 0·04% is left.

If a solution containing sodium and potassium hydroxides is concentrated at 60°C., the potassium hydroxide crystallizes out and leaves the sodium hydroxide in solution.[35] The sodium hydroxide can also be removed by passing sulphur dioxide into the solution to precipitate sodium sulphite.[36] Ion exchange chromatography has been used to concentrate potassium hydroxide from weak solutions,[37] and also to separate it from sodium and lithium hydroxides on a small scale.[38] The method is useful in removing carbonate ions, which are always present in potassium hydroxide which has been exposed to the air. The carbonate ions can be absorbed directly in preference to hydroxide ions by passing a solution down a column of an anion exchange resin.[39] Another method is to add barium hydroxide to precipitate the carbonate, and then pass the filtered solution through a cation exchange resin which retains excess barium ions.[40,41] The eluate solutions are free from barium, chloride, and carbonate ions, provided that they are protected from carbon dioxide. To avoid the difficulty of preserving weak (0·001N.) standard solutions of the hydroxide, they can be produced during the process of titration by passing a weak standard solution of potassium chloride through an anion exchange resin.[42] Free iodine in hydroxide solutions is removed by adding hydrazine.[43]

Potassium hydroxide of analytical quality may contain small amounts of chloride, chlorate, iron and heavy metals as well as carbonate (1–2%) and water. The sodium content can be determined by flame photometry,[44] small amounts of iron (down to 0·001%) by an electrolytic method,[45] and chromium and vanadium by chromatography.[46]

The pure solid can be produced by treating pure potassium metal with pure water or water vapour, and evaporating the solution under reduced pressure in an inert vessel. Complete removal of the water requires fusion in a vacuum, because water vapour dissolves in the molten hydroxide.[83] When exposed to air, the hydroxide rapidly becomes contaminated with water (as hydrates), carbonate and also, apparently, the superoxide KO_2.[52]

Physical Properties of Solid Potassium Hydroxide

The melting point of potassium hydroxide has been given as 406°C.[47,48] and as 404 ± 1°C.,[65] and its lattice energy (at 25°C.) has been calculated to be −153 kg.-cal./mole.[49] The average value of the heat capacity between 19°C. and 100°C. is 16·88 g.-cal./mole/°C.[50] The coefficient of thermal expansion has an average value of about $1{\cdot}9 \times 10^{-4}$ in the temperature range 30° to 130°C.[51] The density at 25°C. has been given as 2·12 g./c.c.[51] and at about 20°C. as $2{\cdot}04_6$ g./c.c.[52]

In the temperature range 0° to 406°C. there are two forms of solid potassium hydroxide, with a transition between them at 240°C.[47] A report that there is a second transition at 375°C.[64] was not confirmed in later work.[47] The structures of the two known forms have been studied by *X*-ray analysis. At about 20°C., the low temperature form (α-KOH), has an orthorhombic unit cell.[52] The structure contains layers in which the potassium and hydroxide ions each have a co-ordination number of 5, and the hydroxide ions of neighbouring layers form zigzag chains through the lattice.

At 300°C. the high temperature form (β-KOH) has a cubic unit cell (a = 5·78A.) like sodium chloride.[53] The hydroxide ions appear to have spherical symmetry, which suggests that they may have some freedom of movement around their lattice positions. The effective radius of the hydroxide ion is 1·53A. The hydrogen atoms were not located in either structure and the transition has not been studied in detail.

The electrical conductivity and viscosity of solid potassium hydroxide have been measured.[54]

From measurements of the decomposition potentials of the fused hydroxide, its free energy of formation at 400°, 500°, 600° and 700°C. was found to be −52·72, −49·47, −46·19 and −40·65 kg.-cal./mole respectively.[55] The specific conductivity, κ, of the fused hydroxide is given by the equation $\kappa = 2{\cdot}52\ [1 +$

$2{\cdot}3 \times 10^{-3}$ (t - 400)] ohms^{-1} where t is the temperature in °C.,[56] and the equivalent conductance was calculated to be 82·4, 93·0, 104·0, 115·6 and 127·2 ohms^{-1} at the temperatures 400°, 450°, 500°, 550° and 600°C. respectively. These values are based on values for the density of the fused hydroxide of 1·717, 1·695, 1·673, 1·651 and 1·629 g./c.c. at these temperatures respectively, and the density may be expressed by the equation $d_t = 1{\cdot}717\,[1 - 2{\cdot}56 \times 10^{-4}\,(t - 400)]$. However, the density at 380°, 400°, 420° and 440°C. has also been given as 1·87, 1·85, 1·83 and 1·81 g./c.c. respectively.[57] The viscosity coefficients at 400°, 450°, 500°, 550° and 600°C. are 0·023, 0·017, 0·013, 0·010 and 0·008 poises.[56]

The refractive index n_λ of the liquid at temperatures near 400°C. is given by the equation $n_\lambda = n_0 - bt \times 10^{-4}$, where t is the temperature in °C. For radiation of wave-lengths 6439, 5893, 5857 and 5589A., n_0 has the values 1·453, 1·479, 1·479 and 1·475 respectively and b the values 1·0, 1·5, 1·33 and 1·33 respectively.[57] At a wave-length of 5893A., the molar refraction is 7·63, 7·66, 7·69 and 7·73 at the temperatures 380°, 400°, 420° and 440°C. respectively.

At 795°C. the vapour pressure of potassium hydroxide was found to be 8 mm.[58] Between 1170° and 1327°C. the vapour pressure is given by the equation:-

$$\log_{10} p_{\mathrm{mm.}} = 7{\cdot}330 - 7103/(T + 273),$$

and the boiling point (under 860 mm. pressure) is about 1322°C.[59] Studies of the mass spectra of the gaseous species produced by the vaporization of potassium hydroxide indicate that, in the temperature range 270°C. to 450°C., the vapour contains mainly the dimer $K_2(OH)_2$.[60] The heat of vaporization is 36 ± 2 kg.-cal. per mole of dimer for the reaction:-

$$2KOH(s) \rightleftharpoons K_2(OH)_2(g)$$

at 353°C. The heat of formation of the hydroxide from potassium atoms and hydroxyl radicals in the gas phase was found to be −87·5 ± 3 kg.-cal./mole from measurements of the electron concentration in flames containing traces of potassium salts.[61]

Potassium Hydroxide in Anhydrous Melts

Anhydrous mixtures of potassium hydroxide with several other ionic solids have been studied. The system NaOH–KOH has a eutectic at the equimolar concentration with a melting point of 170°C.;[62] this mixture can be used as a heat transfer agent.[63] The system LiOH–KOH forms an incongruently melting compound, 2LiOH,KOH.[64] In mixtures with potassium nitrate and nitrite[65] the compounds KOH,KNO_3 and KOH,KNO_2 are formed which melt congruently at 236·5°C. and 177°C. respectively. Sodium nitrate and potassium hydroxide form solid solutions. The system KOH–KCl has two incongruently melting compounds, 2KOH,KCl and KOH,KCl;[64] and the system[66] $KOH–K_2MoO_4$ has the compound $2KOH,K_2MoO_4$ with an incongruent melting point of 580°C.

Several quaternary systems containing potassium hydroxide and two other ions are known and some of their properties have been reviewed.[67] The formation of lithium hydroxide is favoured with equilibria $KOH + LiCl \rightleftharpoons LiOH + KCl$[64] and $Li_2CrO_4 + 2KOH \rightleftharpoons K_2CrO_4 + 2LiOH$.[68] In mixtures with rubidium and caesium nitrates[69] the stable salt pairs are $KOH–RbNO_3$ and $KOH–CsNO_3$. The systems[70] K^+, Na^+, $SO_4^=$, OH^- and[71] K^+, Ca^{++} $SO_4^=$, OH^- have been studied. The fused hydroxide is highly reactive and is a good solvent for ores in analytical work.[72]

Hydrates and the System $KOH-H_2O$

Pickering[73] studied the system $KOH-H_2O$ in the composition range 0–80% potassium hydroxide. The anhydrous hydroxide appeared to be the only stable form above 143° C.; as the temperature is lowered the successive stable forms were KOH,H_2O (75·68%KOH) above 35° C., $KOH,2H_2O$ (60·87% KOH) down to −33° C. and $KOH,4H_2O$ (43·75%KOH) down to a eutectic at −66° C. where the tetrahydrate is in equilibrium with ice and a 30% solution of hydroxide.

Shibata *et al.*,[74] from measurements of the e.m.f. of the cell K,Hg | KOH, nH_2O, KOH,aq.(sat.) | HgO,Hg at various temperatures, found that a hemihydrate $KOH,1\frac{1}{2}H_2O$ (66·13%KOH) is the stable solid form between 33·4°C. and 27·3° C. at which temperatures it is in equilibrium with the monohydrate and the dihydrate respectively. Nizhnik and Lastochkina[75] studied the concentration range 60–97%KOH by thermal analysis and found that the monohydrate, m.p. 143° C., was the only compound formed. Mixtures of the monohydrate with either the dihydrate (up to 10%) or the anhydrous hydroxide (up to 15%), *i.e.*, with a total composition range of 74·2–79·3%KOH, have a relatively constant melting point of about 125°C. The mixture of mono- and di-hydrates behaves almost like a compound.

Cohen-Adad and Michaud[76] studied the complete concentration range, finding a clearly defined isotherm at −65·7° C., which they attributed to a pentahydrate $KOH,5H_2O$, and also, in mixtures containing more than 76%KOH, an isothermal line at 85° C. which showed the existence of another new solid phase whose composition was not determined. Other workers (see the reference 7 quoted in ref. 77) have claimed hydrates with 5, 6, 8 and 18 moles of water per mole of KOH.

Lang and Sukava,[77] in studying the ternary system $KOH-K_2CO_3-H_2O$, found no evidence for either the pentahydrate or that with $18H_2O$. Their results confirm Pickering's work[73] and they suggest that small amounts of carbonate may produce the effects attributed to other hydrates.

Bolte[78] found that the dissociation pressure of the dihydrate at 27·75° C. was 3·6mm. When the system was dehydrated slowly, the pressure fell sharply to 1·54mm. at the composition KOH,H_2O and remained at this value until the composition reached $KOH,\frac{3}{4}H_2O$ when it fell to a very low value. At 31·75° C. the pressure drops occurred at the compositions KOH,H_2O (dissociation pressure 2·1mm.), $KOH,\frac{3}{4}H_2O$ (0·75mm.) and $KOH,\frac{1}{2}H_2O$. The last $\frac{1}{2}H_2O$ is said to be so tightly bound that it gives no detectable vapour pressure at this temperature.

An *X*-ray analysis[79] of the structure of the monohydrate shows that it contains layers of potassium and hydroxide ions linked by water molecules. The oxygen atoms form zigzag chains of the type $-OH-H_2O-OH-$.

The vapour pressure of water over the anhydrous hydroxide at 50°C. was found to be 0·007mm. or less[80] and the pressure at 25°C. was calculated to be not more than 0·002mm. At 25° C., a litre of gas dried by potassium hydroxide, sodium hydroxide or concentrated sulphuric acid contains 0·002mg., 0·16mg. or 0·003mg. of water respectively. Bower[81] measured the relative efficiencies of drying agents and found that at 30° C. a litre of gas dried by potassium hydroxide or sodium hydroxide contains 0·014mg. or 0·80mg. of water, respectively. Drying agents have been reviewed by Yoe.[82] Solid potassium hydroxide is sometimes used to dry organic liquids by contact, but compounds with reactive hydrogen atoms may form ions, or lose the elements of water, or undergo condensation or hydrolysis.

The equilibrium between the hydroxide and water vapour has been studied at temperatures between 300° and 460° C.[83] The concentration of water in the hydroxide depends on its vapour pressure, but later work on this system between 250° and 420° C. with steam pressures up to 300 atm.[84] showed that Henry's law is not obeyed, and that potassium hydroxide has a greater affinity for water than has sodium hydroxide.

Physical Properties of Aqueous Solutions

The solid hydrates do not persist as definite compounds in their aqueous solutions, which contain hydrated potassium and hydroxide ions. *X*-Ray diffraction studies of the solutions[85] indicate that the potassium ion has about four water molecules around it, and the hydroxide ion about four or six. It was shown that the results could also be explained if the hydroxide ion were able to replace a water molecule around the potassium ion. Association of the ions may occur in very concentrated solutions; for example, the saturated solution at 25° C. contains 55% of potassium hydroxide, corresponding to a composition $KOH : 3H_2O$, with less than four water molecules for each potassium ion.

Infra-red absorption spectra of the solutions[86] may also be explained in terms of hydration of the hydroxide ion, whose absorption band has been identified at either $2{\cdot}30\mu$[87] or at $2{\cdot}45\mu$.[88] The bands at $3{\cdot}6-3{\cdot}8\mu$ and $5{\cdot}2\mu$, which are also found in solutions of potassium hydroxide in ethyl alcohol,[89] have been assigned to solvated, undissociated potassium hydroxide 'molecules'.[87] The hydroxide ion gives a Raman line with a frequency shift of about 3603cm.^{-1}.[90] Measurements have been made of the dielectric constants[91,92] and magneto-optical rotation[93] of these solutions.

Mischenko[94] calculated that the sum of the heats of hydration of potassium and hydroxide ions at 25°C. is 195 kg.-cal./mole; of which 80 kg.-cal. are associated with the potassium ion and 116 kg.-cal. with the hydroxide ion.

Three recent determinations of the heat of formation of potassium hydroxide in water at infinite dilution at 25°C. are in good agreement. The values given are $-115{\cdot}21 \pm 0{\cdot}12$,[95a] $-115{\cdot}37 \pm 0{\cdot}10$,[95b] and $-115{\cdot}323 \pm 0{\cdot}010$ kg.-cal./mole.[95c]

Many data on thermodynamic properties of the aqueous solutions are summarized by Harned and Owen.[96]

Measurements of the compressibility coefficients of solutions up to $2{\cdot}5m$. (m is the molality) showed that the apparent molal compressibility varies linearly with $\sqrt{m}$.[97] The standard partial molal compressibility is -81×10^{-4} c.c./bar.[96a]

Densities and apparent partial molal volumes (ϕ_v) have been determined for solutions from 0·5 to 17 molal at 10° intervals between 0° and 70°C.[98a] Some values for the densities are given in Table II. At 25°C. and for concentrations below 5 molal, $\phi_v = \overline{V}_2^{\circ} + 4{\cdot}35\sqrt{m}$. The value of $\overline{V}_2^{\circ}$, the standard partial molal volume at 25°C., has been given as 2·9cc./g.[96b,98b] and also as

TABLE II. - DENSITIES OF AQUEOUS SOLUTIONS OF POTASSIUM HYDROXIDE[98a]

Weight-%	Molality *m*	Densities			
		0°	20°	40°	60°
0	0	0·99982	0·99800	0·99219	0·98330
4	0·7427	1·03849	1·03437	1·02749	1·01822
10	1·9804	1·09650	1·08970	1·08153	1·07174
20	4·4560	1·19542	1·18617	1·17659	1·16610
30	7·6389	1·29840	1·28799	1·27758	1·26653
40	11·8826	1·40765	1·39634	1·38510	1·37335
50	17·8240	1·52565	1·51211	1·50022	1·48802

4·06 c.c./g.[98] Densities and viscosities were measured for solutions up to 8N. in strength at 20°, 30° and 40° C.;[99] these measurements were also made on solutions containing hydroxide and carbonate. Some values for the viscosities are given in Table III.

TABLE III. - VISCOSITY OF AQUEOUS SOLUTIONS OF POTASSIUM HYDROXIDE[99]

Concn. moles/litre	Viscosity (centipoises)		
	20° C.	30° C.	40° C.
0·5N.	1·055	0·846	0·698
1	1·110	0·895	0·743
2	1·239	1·008	0·838
3	1·394	1·143	0·951
4	1·581	1·303	1·081
5	1·811	1·492	1·231
6	2·088	1·718	1·409
7	2·410	1·984	1·616
8	2·791	2·301	1·858

The e.m.f. of the concentration cell $H_2 \mid KOH(m_1) \mid Kx.Hg \mid KOH(m_2) \mid H_2$ has been measured for solutions from 0·05 to 4 molal[100] at 0° to 35° C. and from 0·22 to 17 molal[101] at 0° to 70° C.; earlier work is reviewed in both these references quoted and there is good agreement between the two sets of results. Some values[96c] for the mean ionic activity coefficient $\gamma\pm$ of potassium hydroxide in aqueous solution are given in Table IV. The interpolated value for a 0·1 molal solution at 25° C. is 0·790 ± 0·001, but Guggenheim and Turgeon, who based their calculations on data from experiments with other types of cells, claim that a value of 0·776 is more reliable for this quantity.[102]

TABLE IV. - MEAN IONIC ACTIVITY COEFFICIENTS
OF POTASSIUM HYDROXIDE IN AQUEOUS SOLUTION[96c]

Molality m	$\gamma\pm$			
	0°	20°	40°	60°
0·1	0·796	0·792	0·783	0·772
0·2	0·761	0·756	0·747	0·733
0·4	0·737	0·733	0·722	0·704
1·0	0·757	0·755	0·740	0·713
2·0	0·887	0·884	0·858	0·811
4·0	1·42	1·39	1·30	1·177
8·0	4·48	3·98	3·40	2·82
12·0	13·88	11·10	8·68	6·65
17·0	47·8	34·5	24·4	16·8

The activity coefficient of the hydroxide in a mixed solution with potassium chloride is decreased relatively to its value in the pure aqueous solution ($\gamma\pm_0$), and for concentrations up to 1 molal the relation between the two values is given by the equation $\log(\gamma\pm) = \log(\gamma\pm_0) - \alpha_{12}m_2 - \beta_{12}m_2^2$, where m_2 is the concentration of the chloride.[103]

The relative partial molal heat content of the hydroxide in dilute aqueous solutions is given by the equation $\overline{L}_2 = \overline{L}_2(0° C.) + \alpha T + \beta T^2$, between 0° and 40° C.;[100] and some values of the parameter in this equation are given in Table V. The calculated values of L_2 agree fairly well with those given by Rossini.[104] Values of the relative partial molal heat capacity $\overline{J}_2$ agree with those computed[105] from measurements of heats of dilution, and vary linearly

TABLE V. - RELATIVE PARTIAL MOLAL HEAT CONTENT AND HEAT CAPACITY OF POTASSIUM HYDROXIDE IN AQUEOUS SOLUTION[100]

m	$\overline{L_2}$(0°)	α	β	$\overline{J_2}$(25°C.)
0·05	37	2·4	0·017	3·2
0·1	41	3·6	0·029	5·0
0·15	30	4·7	0·030	6·2
0·25	−1	6·4	0·032	8·0
0·35	−35	8·2	0·034	9·9
0·5	−95	10·4	0·036	12·2
0·75	−180	13·6	0·040	15·6
1·0	−270	16·2	0·043	18·4
1·5	−335	20·6	0·050	23·1
2·0	−381	24·6	0·057	27·4
2·5	−390	28·2	0·063	31·3
3·0	−356	31·5	0·070	35·0
3·5	−335	34·5	0·078	38·4
4·0	−226	37·4	0·081	41·5

with $\sqrt{m}$.[100] The value of the standard partial molal heat capacity $\overline{C^\circ_{p_2}}$ at 25° C. has been given as −30·7 ± 0·5,[96d] −32·1,[105] and −34·4 g.-cal./mole/° C.,[106] although the last value may be slightly in error.[105] The heat capacity of a given solution, in g.-cal. per g. of solution, is equal to $(1000 + m[\overline{C^\circ_{p_2}} + 16{\cdot}1\sqrt{m}])/(1000 + 56{\cdot}1m)$.[106] The relative partial molal entropy of potassium hydroxide in aqueous solutions increases with concentration until the concentration is about 8 molal, above which it becomes almost constant, having the values 8·84, 5·55, 2·25 and −0·73 g.-cal./mole degree at 0°, 20°, 40° and 60° C. respectively.[101]

Electrolysis of Aqueous Solutions of Potassium Hydroxide

The transport number of the potassium ion in solutions in the range 0·01 to 3N. at 25° C. is constant and equal to 0·2633,[107] a value about only half that in solutions of simple uni-univalent potassium salts.

The molal conductivity of potassium hydroxide, measured by a direct current method in very dilute solutions, was found to be 274·9 ohms^{-1}.[108] The equivalent conductance at infinite dilution at 25° C., reported as[109] 270·94 and 272·0 ohms^{-1},[110] is about twice as great as the equivalent conductances of simple uni-univalent potassium salts at 25° C. The excess conductance is associated with the hydroxide ion, whose high limiting ionic conductance of about[109,110] 197·8 is probably due to a proton transfer mechanism of the type $\mathrm{H{-}O{-}\overset{*}{H}} + \mathrm{\bar{O}{-}H} \rightleftharpoons \mathrm{H{-}\bar{O}} + \mathrm{\overset{*}{H}{-}O{-}H}$ as suggested by Bernal and Fowler[111] and supported by recent calculations.[112]

The equivalent conductance decreases with increasing concentration, and for concentrations below 0·06 molar its values at 25° C. are given by the equation $\Lambda = 272 - 121{\cdot}64\sqrt{c} + 141c(1 - 0{\cdot}2274\sqrt{c})$.[110] The conductance in more concentrated solutions at 25° C. is shown in Table VI, and at higher temperatures, in Table VII.[114] The *total* conductivity passes through a maximum at about 6N.[113] The concentration corresponding to this maximum conductivity increases with temperature.[114] The solutions of maximum conductivity at 18°, 55°, 64° and 77° C. contain 27·2, 31·5, 32·0 and 33·0% of potassium hydroxide by weight respectively.

The 'energy of activation' for electrical conductance in potassium hydroxide solutions, which is about 50% of that for sodium hydroxide solutions,[115]

TABLE VI.- EQUIVALENT CONDUCTANCE AT 25°C. OF AQUEOUS SOLUTIONS OF POTASSIUM HYDROXIDE[92]

m moles/1000g. soln.	c g. moles/litre	Λ equivalent conductance at 25°C.
0·06080	0·06081	249·8
0·15064	0·15133	241·5
0·27833	0·28152	234·6
0·50549	0·5167	225·6
1·0204	1·0697	209·0
1·7740	1·9266	187·3
2·2782	2·5338	173·1
3·4544	4·0591	140·9
4·6172	5·726	110·9
5·9823	7·897	79·00
7·5030	10·611	49·35

TABLE VII. - SPECIFIC CONDUCTIVITIES OF POTASSIUM HYDROXIDE SOLUTIONS[114]

Concentration (moles/litre)	Specific conductivity (ohms^{-1})		
	54·8°C.	63·7°C.	77·0°C.
3·8N.	0·853	0·937	1·078
6·1N.	1·004	1·115	1·291
6·9N.	1·014	1·130	1·320
7·4N.	1·016	1·137	1·331
8·8N.	1·006	1·127	1·324
9·2N.	0·950	1·108	1·312
10·6N.	0·928	1·058	1·264

is less than the 'energy of activation' associated with viscous flow,[116] and this could be explained if part of the conductivity involves proton transfers.

The molal conductance increases with temperature and also with pressure[117] up to about 3000 atm., but is almost constant between 3000 and 12000 atm. The excess conductance, relative to a solution of potassium chloride of the same concentration and under the same conditions, itself increases with temperature and pressure, and is proportional to the rate of the proton exchange reaction given above. The conductivity has been measured at temperatures up to 700°C. under pressures of up to 2800 atm.[118] The ionic mobility increases with pressure both in the liquid solutions and in the mixture above the critical point. The dissociation constant of potassium hydroxide in supercritical water at 500°C. is only $1{\cdot}9 \times 10^{-5}$ mole/litre under a pressure giving a density of 0·3 g./c.c., and increases to $3{\cdot}4 \times 10^{-2}$ mole/litre at 0·8 g./c.c.; the corresponding degrees of dissociation are 0·31 and 0·9 respectively. The dissociation into ions *decreases* with increasing temperature at a given pressure; in the temperature range 400° to 700°C. the energy of dissociation is −6 kg.-cal./mole, and the change in entropy, −76 g.-cal./mole degree.

Gaseous hydrogen and oxygen can be manufactured by the electrolysis of potassium hydroxide solutions,[119] and the process is more efficient if the solutions are compressed.[120] Pure solutions of about 30% concentration are used,[121] and the cell electrodes are designed to allow a maximum current density.[122] The evolution of hydrogen at an iron anode has been studied.[123,124] Potassium hydroxide is the electrolyte in some alkaline storage batteries and primary cells[125] and also in fuel cells.[126] It is also used in cells which produce molybdate, permanganate and chromate ions by the anodic oxidation of molybdenum,[127] manganese steel[128] and chromium steel[129] respectively.

Some Chemical Reactions of Potassium Hydroxide

Most reactions of potassium hydroxide are those of the hydroxide ion and are given by other strong bases.

The corrosion of iron by hot strong potash solutions is reduced by adding alkali metal nitrates and nitrites to the melt.[130] Nickel and chromium steels[131,132] and aluminium bronze[133] are more resistant, and so is zirconium.[134]

The rate of reaction with noble metals is greatly increased by the presence of gaseous oxygen, up to a maximum at 20% concentration in a gaseous mixture, and the attack is greatest when there is also a 25% concentration of water vapour.[135] At 410°C., in air containing 25 mole-% of water, the rates of attack on gold, silver and platinum are 18, 6·35 and 1200g. per square metre per day. Nickel is attacked at about the same rate as silver under these conditions. The corrosion of gold is reduced about one hundredfold if the metal is alloyed with palladium.[136] Some synthetic polymers such as polyethylene, polystyrene and polytetrafluoroethylene are very resistant to alkalis at temperatures below their softening points. Amber[137] is resistant to a 50% solution at 100°C. There are two reviews on corrosion by fused hydroxides.[138,139] Potassium hydroxide vapour corrodes siliceous materials in retorts at about 1000°C.[140]

The hydroxides of several metals such as aluminium, tin, zinc and chromium dissolve in aqueous potassium hydroxide to give solutions which contain the colloidal hydroxide or complex ions or both.[141] Zinc hydroxide is partly colloidal in solutions up to 6N. in potassium hydroxide, but above 8N. all the zinc is present as complex ions.[142] A study of the behaviour of zinc anodes in concentrated potassium hydroxide solutions indicates that the ion $Zn(OH)_4^=$ is formed,[143] and it was later found[144] that for the reaction $ZnO + 2OH^- + H_2O \rightleftharpoons Zn(OH)_4^=$, the equilibrium constant is $100 \pm 2 \times 10^{-4}$ and the change in free energy is −205·2 kg.-cal./mole. A trihydroxy ion is also formed in more dilute solutions,[144] and for the reaction $ZnO + OH^- + H_2O \rightleftharpoons Zn(OH_3)^-$, the equilibrium constant is 6×10^{-4} and the change in free energy, −165·9 kg.-cal./mole. A claim that a hexahydroxy complex is formed[145] is said[144] to be in error because the results were expressed in concentrations, whereas calculations based on activities show that only a tetrahydroxy ion exists. The polarographic behaviour of these ions has been studied.[146]

The formation of basic ions by aluminium in potassium hydroxide solutions has been studied by measurements of freezing points,[147] conductivity[148] and the e.m.f. of alkaline cells.[149] Ferric sulphate forms a complex polynuclear hydroxysulphate anion.[150] Ferric hydroxide dissolves in potassium hydroxide solutions with greater ease when chromium hydroxide is also present.[151] In the concentrated boiling solutions, manganous hydroxide is oxidized by gaseous oxygen to trimanganese tetroxide, potassium permanganate and $2K_2O,Mn_2O_3,2MnO_2$, depending on the degree of oxidation.[152] In strong solutions, the hydroxide ions are oxidized to oxygen by ferricyanide ions[153] and by permanganate ions.[154]

When nitrosyl chloride and nitrogen tetroxide are hydrolyzed by potassium hydroxide, some nitric oxide is formed.[155] With solid potassium hydroxide, nitric oxide reacts at room temperature over a period of several days to give nitrous oxide, nitrogen and potassium nitrite, and the solid hydroxide also appears to catalyze the thermal decomposition of nitrous oxide.[156] Slow evaporation of solutions containing 2 moles of hydrogen peroxide to one mole of the hydroxide gives the compound[157] $K_2O_2,2H_2O_2$ which decomposes above 0°C. The compound CF_3I reacts to give CF_3H.[158]

Although the heat of neutralization of potassium hydroxide by acids at infinite dilution has a constant value of −13,650 g.-cal./mole at 20°C.,[159] the measured heats of mixing depend on the concentrations of acid and base, partly owing to changes in the partial molal heat capacities of the resultant solutions.[160] They have been studied in detail[161,162] for the neutralization of potassium hydroxide by nitric acid. Similarly, the heat of neutralization of sulphur dioxide by potassium hydroxide has a minimum value when the solution is about 0·2M. in potassium sulphite.[163] This is explained[164] by the difference in the heats of dilution of potassium hydroxide and sulphite. The rate of absorption of sulphur dioxide gas by potash solutions has been studied.[165]

Reaction of Potassium Hydroxide with Carbon Dioxide.

Solutions of potassium hydroxide are often used to remove carbon dioxide from gases. The kinetics of the reaction $OH^- + CO_2 \rightleftharpoons HCO_3^-$ have been studied;[143] the velocity constant is given by the expression $\log k = 13{\cdot}635 - \frac{2895}{T}$. The heat of reaction is −10,690 g.-cal. ± 1% at 22°C.[167]

The overall rate of absorption depends on physical absorption accompanied by chemical reactions.[177] The amount of carbon dioxide absorbed increases with the viscosity of the solution[168] but the rate of absorption is inversely proportional to the viscosity.[169,170] The rate increases with hydroxyl concentration to a maximum at about 28% of potassium hydroxide[171] although the rate increases only slowly above 4% and the maximum has also been claimed for 2N. solutions.[172] The rate depends on the concentration gradients of carbon dioxide in the liquid, which is itself determined by the hydroxyl ion concentration.[170] The rate also depends on the concentration of carbon dioxide in the gas phase[173] and on the extent of contact between gas and liquid.[172] Equilibrium at the interface between gas and liquid is reached very quickly, and the diffusion of molecules of carbon dioxide into the liquid as the reaction proceeds may determine the overall absorption rate.[174] Several equations have been given[170,172,173,175,176] which represent the overall rate of absorption in different types of apparatus, and a graphical method for designing such apparatus has been described.[177] Useful reviews of previous work on this subject have been published.[169,170,173]

Some data have been given on the conditions required for the complete absorption of carbon dioxide in gas pipettes.[178] In the determination of small amounts of carbon dioxide[179] it was found that pellets of potassium hydroxide were more efficient when moist than when absolutely dry.

In the system $KOH–K_2CO_3–H_2O$[77,180] there is no evidence of compound formation between the two salts. The total solubility varies only slightly with their relative amounts. Some values of the ratio $\%KOH:\%K_2CO_3$ in saturated solutions at 25°C. are 10·8:39·5, 22·8:24·9, 37·0:11·1 and 50·4:2·9. In these solutions, the viscosity is greater and the conductivity less than in the solution of the single hydroxides.[181] Viscosity and density data for the mixed solutions have been given.[99] Since the carbonate is a common impurity in the hydroxide, solution properties of the hydroxide are sometimes determined by measuring their values in mixed solutions of known composition and extrapolating the results to zero concentration of carbonate.

Miscellaneous Phase Equilibria.

Phase equilibria are known (in part) for systems containing potassium hydroxide, water and the following compounds: sulphur dioxide,[182] potassium chloride,[183,184] potassium molybdate,[185] potassium iodate,[186] potassium tartrates,[187] uranyl nitrate[188] and phosphoric acid.[189-191]

The equilibrium between potassium hydroxide and calcium sulphate is important in the setting of cement[192] and the strength of concrete is increased by adding to the mixture 0·2 to 1% of the hydroxide with twice this amount of potassium sulphate,[193] although the composition of the solid phase may not be altered.[194]

Potassium hydroxide undergoes base exchange with clay minerals,[235] and, by treatment with a normal solution of the hydroxide montmorillonite is changed into illite.[236]

Potassium hydroxide is insoluble in liquid ammonia[195] and when it is added to strong aqueous solutions of ammonia, they separate into two layers.[196] Its 'salting out' effect has been studied also with aqueous solutions of pyridine and dioxan,[197] acetone[197,198] and triethylamine.[199]

At 28°C., 100 c.c. of ethyl alcohol will dissolve 29·0 g. of the hydroxide to give a solution with a density of 1·04 g./c.c. and 100 c.c. of methyl alcohol will dissolve 40·3 g. to give a solution with a density of 1·14 g./c.c.[200] The preparation[201-203] and preservation[204] of the solutions in ethyl alcohol have been described, and measurements made of the conductivity of solutions of the hydroxide in alcohols, aniline and pyridine.[205]

Reactions of Potassium Hydroxide with Organic Compounds.

Solutions of potassium hydroxide in organic liquids do not always contain only solvated potassium and hydroxide ions; in the alcohols, for example, alkoxide ions are produced by the reaction $OH^- + ROH \rightleftharpoons RO^- + H_2O$. The hydroxide will also form salts with weak acids like pyrroles[206] and fluorene,[207] and it can be used as an absorbent for acetylene.[208] It will substitute hydroxyl groups for hydrogen in compounds like nitrobenzene[209] and anthanthrone.[210] The fused hydroxide reacts with alcohols, aldehydes, ketones and esters to give potassium carbonate and hydrogen and/or methane.[211] Ethers and amines are not attacked, but glycol, glycerol[212] and sugars and cellulose[213] are also completely decomposed. *cyclo*Hexanol is oxidized to caproic acid by the fused hydroxide,[214] and hot solutions of the hydroxide will also dehydrate aliphatic hydroxy compounds. A good absorbent for oxygen is a solution containing 18% of potassium hydroxide, 15% of pyrogallol and 67% of water.[171]

Under mild conditions, potassium hydroxide forms solid addition compounds with some substances containing hydroxyl groups. With the potassium salts of tartaric acid, the compounds known[187,215] are KOH,K(*d*-tartrate),$1\frac{1}{2}H_2O$, KOH,K(mesotartrate),$3H_2O$ and K(mesotartrate),$2\frac{1}{2}$KOH, $3H_2O$. With glucose[216] and galactose[217] 1:1 compounds are formed; in the former the reducing group of the sugar is involved in the bonding. With disaccharides, cellobiose gives compounds with one and two moles of hydroxide,[216] maltose with one, two and three moles,[216] and lactose gives a mixture of the 1:2 and 2:3 compounds.[217] The effects in solution are complicated because the alkali disturbs the equilibrium among the tautomeric forms of the sugars and also decomposes them,[218,219] although it was found that sucrose reduces the concentration of hydroxyl ions in aqueous potassium hydroxide.[220] *X*-Ray studies show that polyvinyl alcohol forms molecular compounds with alkalis.[221] Cellulose forms compounds in which the ratio $C_6H_{10}O_5$:KOH has the values 2:1, 3:2, 4:3 and 1:1,[222,223] and the structure of these alkali celluloses has been discussed.[224]

Cotton cellulose absorbs the ions in potassium hydroxide solutions and swells,[225-227] and when the mixture is treated with carbon disulphide, the potassium salt of cellulose xanthate is produced.[228]

Addition compounds are also found with inulin and anhydrosugars,[229] cyclic imides[230] and creatinine.[231]

Potassium hydroxide is absorbed by gelatin[232] and by other colloidal electrolytes in solution, a process which affects the apparent neutralization point when the hydroxide is used to titrate polymeric acids like polyacrylic acid[233] and polymethacrylic acid.[234]

Uses

In addition to its uses as an electrolyte in cells and as an absorbent for carbon dioxide, potassium hydroxide, either anhydrous or in solution in water[237]

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or alcohols, will act as a catalyst in hydrolysis and condensation reactions[238] such as the reaction of formaldehyde with phenols[239] and the polymerization of siloxanes.[240] It improves the performance of metal oxide catalysts in dehydrogenation reactions[241] and in the hydrogenation of carbon monoxide.[242] In the latter reaction, the hydroxide may act by preserving on its surface the methylene radicals which later combine to give hydrocarbon chains.[243] When added to Raney nickel catalysts[244] the hydroxide inhibits the dehydration process without affecting the dehydrogenation.

Concentrated aqueous potassium hydroxide extracts mercaptans from petroleum distillates;[245-247] it is more efficient than sodium hydroxide and requires the addition of a smaller amount of methyl alcohol to prevent solidification. High-temperature lubricants suitable for use in the extrusion pressing of steels are made from potassium hydroxide with mica or molybdenum sulphide.[248]

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SECTION L

POTASSIUM FLUORIDE

By W. H. LEE and M. F. C. LADD

Preparation

No new laboratory-scale preparations have been reported, but the following methods have been proposed for the industrial production of potassium fluoride. Treatment of a silicate mineral, e.g. felspar, with steam and silicon tetrafluoride at 500°–600° yields potassium fluoride, which may then be extracted with water.[1] A method used in the preparation of sodium fluoride – by treating a mixture of sodium carbonate and silicofluoride, Na_2SiF_6, with caustic soda – is said to be applicable to the preparation of potassium fluoride;[2,3] it is thought that the greater solubility of the potassium salt may, however, render its separation more difficult. Potassium fluoride may be obtained by fusing calcium fluoride with silica and caustic potash or potassium carbonate, the mixture of potassium fluoride and silicate being extracted with water; this method has now been improved by treating the solution with hydrofluoric acid, hydrofluosilicic acid, or potassium silicofluoride, K_2SiF_6, to convert the potassium silicate first formed into potassium fluoride and silica.[4] Fusion of calcium fluoride and potassium carbonate, in the mol. ratio 1:2, yields potassium fluoride, which again may be extracted with water.[5] Freshly prepared, molten potassium sulphide is converted into the fluoride by mixing with a solution of hydrogen fluoride, or of sodium fluoride, out of contact with air;[6] alternatively, the sulphide may be treated with sufficient hydrofluoric acid to give a solution of the acid fluoride, KHF_2, containing free HF. Evaporation and crystallization recovers the acid fluoride, which may be decomposed by heating.[7] Solutions of potassium fluoride containing thionates may be purified by treatment with hydrochloric acid under pressure at 300°. The fluoride is extracted with water.[7a]

Potassium fluoride has been prepared by treating solid potassium chloride with excess of gaseous hydrogen fluoride at quite low temperatures; it is stated that 15° is suitable. The resulting product is heated in order to remove excess of hydrogen fluoride.[7b] The treatment of potassium halides with fluorine leads to the formation of compounds of higher fluorine content than the normal fluorides.[8] The formula KF_2 is suggested for one such compound prepared in this manner, and some of its properties have been discussed.[9] The separation of ammonium and potassium fluorides from a mixture may be accomplished by passing ammonia into the solution, the ammonium salt being precipitated.[10]

The acid salt, KHF_2, has been dehydrated by treatment with fluorine.[11] This salt is often used as the electrolyte in cells producing fluorine, and it is important that iron, present as an impurity, should be removed as completely as possible. This has been effected by treatment with sodium fluoride, when the triple salt, $NaF,2KF,FeF_3$, is precipitated, reducing the iron content to a few tenths of 1%.[12]

Physical Properties

The lattice constant and density of potassium fluoride have been re-determined, with the results listed in Table I:-

TABLE I. - LATTICE CONSTANT AND DENSITY OF POTASSIUM FLUORIDE

d	*a*	*t*°C.	Ref.
2•5283	5•333	-	13
2•505	-	25	14
2•369	-	18•6–19•2	15
2•524	5•347	26	16
2•096	5•34	21•5	Mellor, II, 513

These values differ from those previously recorded and given in the last line of the Table, and it seems probable that the best value for the lattice constant is 5•347A.

The lattice energy has been re-calculated[17,18] and the values deemed reliable are listed in Table II:-

TABLE II. - LATTICE ENERGY OF POTASSIUM FLUORIDE

U (kg.-cal./mol.)	193	193	192	192
Ref.	17	18	18	Mellor, II, 512

The first value in this Table was obtained on the assumption of basic ionic radii. The second value results from application of a modified Born–Haber cyclic process, and the third from consideration of an electrostatic model, allowing for dipole–dipole and dipole–quadrupole interactions. Oriented overgrowths of potassium fluoride are produced on crystals of sodium chloride but not on crystals of silicon carbide;[19] the theoretical reasons for this have been discussed. Similar overgrowths on potassium chloride, potassium bromide and lithium fluoride, have subsequently been reported.[20]

The crystal structure of the hydrate, $KF,2H_2O$, obtained by crystallization from the saturated aqueous solution, has been determined by *X*-ray diffraction. The crystals are orthorhombic,[21] with $a = 4{\cdot}06$A., $b = 5{\cdot}15$A., $c = 8{\cdot}17$A.

A study of the structure of the acid fluoride, KHF_2, by neutron diffraction has shown that the hydrogen atom occupies a central position in the linear F – H – F ion to within 0•1A.[22,23] and that the F – F distance is the sum of the atomic and ionic radii of fluorine.[24,25]

Vapour density determinations at 1550° show that potassium fluoride consists of simple molecules in the vapour phase.[26] The vapour pressure of the fluoride has been measured at a number of temperatures[27] and the results, listed in Table III, accord with the formula:-

$$\log P\ (\text{atm.}) = -41900/4{\cdot}57T + 5{\cdot}138$$

TABLE III. - VAPOUR PRESSURE OF POTASSIUM FLUORIDE

P mm.	*t*°C. expt.	*t*°C. calc.
249•8	1351	1352
526•2	1454	1451
539•1	1457	1455
759•6	1504	1505
759•6	1503	1505

The melting point is recorded as 846°, and the boiling point as 1505°C.

The heat of formation of potassium fluoride at 25° is 134•5 kg.-cal./mole.[28] The entropy of fusion is 5•52 e.u., from which it is deduced that the salt is fully ionized in the fused state.[29]

The molar conductivity, Λ_t, of fused potassium fluoride at temperature $T°$

has been shown to follow the relationship:-

$$\Lambda_t = 101{\cdot}8 + 0{\cdot}3163(t - 900),$$

within the range $t = 863°$ to $t = 975°$C.[30] The conductivity of fused salt mixtures with sodium chloride has been determined, as listed in Table IV.[31]

The decomposition potentials of fused potassium fluoride have been measured:-[32]

$t°$	900	940	980
volts	2·13	2·00	1·70

TABLE IV. - ELECTRICAL CONDUCTIVITIES OF FUSED POTASSIUM FLUORIDE AND MIXTURES WITH SODIUM CHLORIDE

KF									
$t°$	860	880	900	950	980	1000			
κ_t	4·14	4·19	4·28	4·54	4·79	4·77			
2KF,NaCl									
$t°$	710	750	780	800	820	860	885	900	930
κ_t	2·30	3·20	3·38	3·47	3·62	3·71	3·92	4·19	4·35
KF,NaCl									
$t°$	720	770	800	840	910	930	960		
κ_t	2·67	2·98	3·25	3·68	3·95	4·22	4·34		
KF,2NaCl									
$t°$	710	760	815	900	940	970	1000		
κ_t	2·27	2·64	3·29	3·80	4·02	4·40	4·50		

For a series of halides of a given alkali metal, the dielectric strength is a linear function of the heat of formation of the solid and gaseous states of the compound: the value for potassium fluoride is $2{\cdot}0 \times 10^6$ volts/cm.[33]

The molar refraction of potassium fluoride dihydrate, $R_{KF,2H_2O}$, is 11·62. Since R_{KF} is 5·06, the refraction contribution of the water of crystallization, R_{H_2O}, is 3·28.[34]

Some thermodynamic properties of the acid fluoride, β-KHF_2, have been investigated, and are listed in Table V.

TABLE V. - THERMODYNAMIC PROPERTIES OF β-KHF_2

$T°$K.	Process	ΔH, kg.-cal./mole	ΔS, e.u.
469·2	$\alpha \rightarrow \beta$ transition	2·68	5·7
511·9	formation	1·58	3·1
500·0	decomposition [KHF_2(solid β) $\rightarrow$ KF(solid) + HF (gas)]	18·5	-

From a consideration of these, and other, data, the value 2·67 ± 1 kg.-cal./mole, for the ΔH $\alpha \rightarrow \beta$ was adopted. From the fact that $\Delta S_{\text{decomp.}}$ tends to zero as $T \rightarrow 0°$K., it is concluded that the height of the potential barrier between the two minima is small.[35]

The hydrogen bond in KHF_2 has been further considered. From a study of infra-red absorption and reflexion spectra, a double-minimum potential energy curve for the F – H – F ion, such as is found for the O – H – O system in ice, was postulated. This follows from the assignment of two absorption lines, at 1222 cm.$^{-1}$ and 1450 cm.$^{-1}$, to the hydrogen frequency of the HF_2^- ion. On this basis, the resonance energy is calculated as 0·04 kg.-cal./mole, compared with a total H-bond energy of 30–50 kg.-cal./mole; the F – F distance is 2·26A., as compared with twice the ionic radius of the F^- ion, 2·70A.[36] This assignment of the above frequencies has, however, been questioned. The peaks at 1222 cm.$^{-1}$ and at 1450 cm.$^{-1}$ were taken to represent the ν_2 and ν_3 fundamentals, and not the doubling of ν_3; on this basis, no pronounced double-minimum potential energy curve is to be expected, and this view is supported by heat-capacity measurements at low temperatures.[37]

A similar conclusion has been reached from a study of the temperature coefficient of dielectric permittivity. The value $+2 \times 10^{-4}$, between 80°K. and 300°K.,[38] differs greatly from that deduced for the double-minimum model, viz. -10^{-2} to -10^{-3}.

Evidence for the high degree of ionicity of the H – bond in HF_2 is afforded by a study of the Raman spectrum of solutions of KHF_2.[39]

Turning to a consideration of aqueous solutions of potassium fluoride, the refractive indices have been measured by an interferometric technique.[40]

Table VI lists the normality, c; the difference between refractive indices of solution and solvent, δn; and the refractivity-function, ψ, defined by $\psi = 560{\cdot}68\ \delta n/c$. The refractive index of water, at temperature t°, is given by:-

$$n_t^D = 1{\cdot}333000 - 10^{-5}[0{\cdot}124(t - 20) + 0{\cdot}1993(t^2 - 400) - 5 \times 10^{-6}(t^4 - 160{,}000)]$$

TABLE VI. - REFRACTIVE INDICES OF AQUEOUS SOLUTIONS OF POTASSIUM FLUORIDE AT 18°

c	$10^6\ \delta n$	ψ
0·002	4·2	4·08
0·0016	3·7	3·31
0·0013	3·0	4·50
0·001	2·4	4·65
0·0009	2·2	4·7
0·0008	1·9	4·6
0·0007	1·7	4·7
0·0006	1·4	4·6
0·0005	1·2	4·7
0·0004	1·0	4·8
0·0003	0·7	4·6
0·0002	0·5	4·8

From the non-linearity of the relationship $10^6\delta n/\sqrt{c}$ below $c = 0{\cdot}0007$, it is concluded that a change in the ionic forces occurs at this concentration: ψ appears to be an 'independent' ionic function, like electrical mobility:-

$$\left.\begin{array}{l}\psi_{KF} - \psi_{NaF} = 0{\cdot}8\\ \psi_{KI} - \psi_{NaI} = 0{\cdot}8\end{array}\right. i.e.\ \psi_{K^+} - \psi_{Na^+} = 0{\cdot}8$$

$$\left.\begin{array}{l}\psi_{KI} - \psi_{KF} = 8{\cdot}9\\ \psi_{NaI} - \psi_{NaF} = 8{\cdot}9\end{array}\right. i.e.\ \psi_{I^-} - \psi_{F^-} = 8{\cdot}9$$

At 25°, the solubility of potassium fluoride is 30·49 moles per 100 moles of water; the heat of solution, at infinite dilution, is 5·912 kg.-cal./mole at this temperature.[41] The integral heats of dilution, for solutions in water and in D_2O, are recorded in Tables VII and VIII.[42]

An equation is proposed for the evaluation of the standard free energies of hydration of alkali halides, which gives for potassium fluoride the value 180 kg.-cal./mole.[44] The equation uses thermodynamic data from the literature; the value 31·5 kg.-cal./mole is taken for one-half the dissociation energy of fluorine, whereas the present accepted value is 18·3 kg.-cal./mole.[45]

TABLE VII. - INTEGRAL HEATS OF DILUTION, V_m, OF POTASSIUM FLUORIDE SOLUTIONS IN WATER AT 25°C.

Concn., mol./100 mol. soln.		V_m
Initial	Final	g.-cal./mole
28·02	9·47	1326
15·94	5·99	463
9·16	1·96	116·6
6·00	2·00	34·91
2·02	0·45	27·68
0·555	0·102	58·3

TABLE VIII. - INTEGRAL HEATS OF DILUTION OF POTASSIUM FLUORIDE SOLUTIONS IN D_2O, AT 25°C.

% D_2O	Concn., mol./100 mol. solvent		V_m, observed	V_m, mean pure D_2O
	Initial	Final		
94·7	25·63	9·45	1068·5	1074
94·7	25·6	6·015	1133	1136
94·5	17·6	6·09	503	507·5
94·3	9·4	2·01	59·4	64
94·3	1·95	0·551	−17·3	−19
94·2	0·551	0·101	66	65

Further heat data, for solutions of potassium fluoride in water, are listed in Table IX.[43]

TABLE IX. - HEAT DATA FOR THE SYSTEM POTASSIUM FLUORIDE-WATER AT 25°C.

Process	ΔH_{25°, kg.-cal./mole
Heat of solution of KF, infinite dilution	+4·244
Heat of solution of KF, sat. soln.	+2·415
Heat of dilution of KF, sat. soln.	+0·185
Heat of hydration, KF → $KF,2H_2O$	+5·912
Heat of solution of $KF,2H_2O$, inf. diln.	−1·668
Heat of solution of $KF,2H_2O$, sat. soln.	−3·497
Heat of dilution of $KF,2H_2O$, sat. soln.	−4·367

The heat of hydration ΔH_h of potassium fluoride is found to be 193 kg.-cal./mole.[46] The assumption of equal heats of hydration of K^+ and F^-, made by Bernal and Fowler,[47] is rejected, the authors choosing $\Delta H_h(Cs^+)$ equal to $\Delta H_h(I^-)$; on this basis, they calculate the individual heats of hydration for K^+ (ΔH_h = 80 kg.-cal./mole), and F^- (ΔH_h = 113 kg.-cal./mole).

Vapour pressure data have been employed to study the degree of dissociation α of the potassium halides, in concentrated aqueous solutions and the hydration-numbers of the individual ions.[48] For potassium fluoride:-

Concn., moles per litre of water	Concn., moles per litre 'free' water	α	Moles of water bound by ions
4–8	6·31–18·44	0·425–0·328	20·4–31·5

The hydration-numbers of the ions are $K^+ = 4$ and $F^- = 8$.

The high-temperature hydrolysis of the potassium halides has been studied; for the reaction:-

$$KF(s) + H_2O(g) = KOH(s) + HF(g)$$

pK, at 25°, = 19·90. For the reaction:-

$$KF(l) + H_2O(g) = KOH(l) + HF(g)$$

pK at 1000° = 5·1. For the reaction:-

$$2KF + H_2O(g) + \tfrac{1}{2}O_2 = 2KOH + F_2$$

pK at 25° = 95·6. The stability of potassium fluoride against high-temperature hydrolysis is less than of the other potassium halides; the contrary is true for lithium fluoride.[49]

Current-voltage relationships in the electrolysis of aqueous solutions of potassium fluoride have been determined, using bright platinum electrodes.

TABLE X. - CURRENT-VOLTAGE RELATIONSHIPS FOR AQUEOUS POTASSIUM FLUORIDE

t°C.	Normality, KF	First break in I/V curve, volts	Second break in I/V curve, volts
0	0·1	1·62 ± 0·05	2·55
25	0·1	1·62 ± 0·05	2·35
0	1·0	1·62 ± 0·05	2·37
25	1·0	1·62 ± 0·05	2·23

The initial break, at 1·62 volts, is said to correspond with the decomposition potential of water in the solution with bright platinum electrodes. The potential up to the second break includes the opposition of the resistance of the solution, reversible decomposition of water, and the hydrogen and oxygen overvoltages for smooth platinum.[50]

The lowering of the eutectic temperature of potassium nitrate-water mixtures, by addition of potassium fluoride, has led to adoption of the formula KF, rather than K_2F_2, for this salt. Results with KHF_2 imply complete dissociation into K^+ and HF_2^-, with further partial dissociation into HF, and F^- on dilution.[51,52]

Viscosities and diffusion coefficients of aqueous solutions of potassium fluoride are given in Table XI. The product of viscosity, η, and diffusion coefficient, D, is found to be approximately constant.[53]

TABLE XI. - VISCOSITIES AND DIFFUSION COEFFICIENTS IN AQUEOUS SOLUTIONS OF POTASSIUM FLUORIDE AT 20°

Concn., wt.%	$d^{20°}_{4°}$	η, c.g.s. units	10^5D, cm.^{2}, sec.$^{-1}$	$10^7\eta D$
33·8	1·3054	0·0267	1·58	4·22
40·5	1·3815	0·0362	1·42	5·14
43·7	1·4195	0·0417	1·33	5·55
45·9	1·4379	0·0470	1·10	5·17
47·4	1·4564	0·0513	1·04	5·34
47·5	1·4639	0·0516	1·00	5·16

The magneto-optical rotations for the D-lines for aqueous solutions at various concentrations have been measured.[54] The data for potassium fluoride are recorded in Table XII.

$[\omega_2]$ is derived from the experimental values of $[\omega]$ by means of the equation:-

$$[\omega] = r_1[\omega_1] + r_2[\omega_2];$$

where $[\omega_1]$ and r_1 apply to water.

Magnetic susceptibility measurements on aqueous solutions of potassium fluoride at 20° give $\chi_m = -24{\cdot}1 \times 10^{-6}$,[55] which agrees closely with $\chi_m = -24{\cdot}08 \times 10^{-6}$, subsequently determined.[56] Values are further deduced for the fluoride ion, $\chi_m = -8{\cdot}2 \times 10^{-6}$ (dissolved), and $\chi_m = -7{\cdot}7 \times 10^{-6}$ (free), and for the potassium ion, $\chi = -16{\cdot}3 \times 10^{-6}$ (dissolved and free).

TABLE XII. - MAGNETO-OPTICAL ROTATIONS FOR POTASSIUM FLUORIDE SOLUTIONS AT 25°

r_2 g. solute/ 100g. soln.	$d^{25°}_{4°}$	Magnetic rotn. χ	Verdet's const. ω	sp. rotn. $[\omega]$	$[\omega_2]$, solute	$M[\omega_2]$
0	0·99707	12·698	0·013075	0·013113	–	(0·275)
12·58	1·1087	12·97	0·01336	0·01205	0·0047	0·27
15·19	1·1328	13·00	0·01339	0·01182	0·0046	0·27
18·68	1·1663	13·05	0·01344	0·01152	0·0046	0·27
22·14	1·2004	13·09	0·01348	0·01123	0·0046	0·27
26·41	1·2441	13·08	0·01347	0·01083	0·0045	0·26
29·33	1·2746	13·05	0·01344	0·01054	0·0043	0·25

Potassium fluoride dissolves in hydrofluoric acid and the specific and equivalent conductances have the values given in Table XIII.[57]

TABLE XIII. - ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF POTASSIUM FLUORIDE IN HYDROGEN FLUORIDE AT −15°

KF concn., mol./litre	κ	Λ
0·5	0·0863	172
0·24	0·0488	203
0·115	0·0258	225
0·055	0·0133	241
0·026	0·00663	251
0·013	0·00321	255
0	–	260

From these data it is inferred that, in 0·5 mol./litre solution in hydrogen fluoride, potassium fluoride is 65% dissociated.

The vapour pressures of such solutions have been measured, and may be represented by the equation:-

$$\log P = 2{\cdot}0733 - 4244/T + 0{\cdot}2975c + 47{\cdot}94c/T - 0{\cdot}003785c^2,$$

over the ranges c = 38–44 wt.% HF, and temperatures of 70°–150° C.[58]

From an analysis of cryoscopic and ebullioscopic data, for the system potassium fluoride–hydrogen fluoride, equations have been deduced relating the activities of the components to the concentration of the solutions.[59]

The solubility of potassium fluoride in bromine trifluoride is compared with that for water and hydrofluoric acid solvents in Table XIV, giving the solubilities, in mol-fractions of solute species, in bromine trifluoride, water and anhydrous hydrogen fluoride respectively.[60]

At 20°, the solubility of potassium fluoride in phosphorus oxychloride is 0·40 g./l.,[61] and this solution has a specific conductance of $2{\cdot}6 \times 10^{-5}$ ohm^{-1} cm.$^{-1}$

Solubility measurements have also been made in certain organic solvents with the results recorded in Tables XV[62] and XVI:-[63]

TABLE XIV. - SOLUBILITY OF POTASSIUM FLUORIDE IN BROMINE TRIFLUORIDE, WATER AND HYDROGEN FLUORIDE

t°C.	m_{KBrF_4}	m_{KF}	m_{KHF_2}
12	-	-	0·129
25	0·1759	0·242	-
70	0·205	-	-

TABLE XV. - SOLUBILITIES OF POTASSIUM FLUORIDE IN METHYL, ETHYL AND BUTYL ALCOHOLS

Solvent	20°	30°	40°	45°	50°	55°
Methyl alcohol	10·6	9·3	8·3	7·2	6·9	5·1
Ethyl alcohol	8·4	7·6	5·4	3·9	1·8	0·8
Butyl alcohol	insol.	-	-	-	-	insol.

The units of concentration are moles per mole of solvent, and the experimental results have been multiplied by 10^4.

TABLE XVI. - SOLUBILITIES OF POTASSIUM FLUORIDE IN METHYL ALCOHOL AND METHYL CYANIDE

Concn. units	MeOH		MeCN	
	18°	25°	18°	25°
g./100g.	$10{\cdot}0 \times 10^{-3}$	$10{\cdot}2 \times 10^{-3}$	$3{\cdot}6 \times 10^{-3}$	$2{\cdot}4 \times 10^{-3}$
mol./l.	$1{\cdot}35 \times 10^{-4}$	$1{\cdot}38 \times 10^{-4}$	$4{\cdot}8 \times 10^{-4}$	$3{\cdot}2 \times 10^{-4}$

The solubility of potassium fluoride in aqueous acetone at 18° has been determined. Values of relative solubility (solubility in mixed solvent/solubility in water) are shown in Table XVII.[63a]

TABLE XVII. - THE SOLUBILITY OF POTASSIUM FLUORIDE IN AQUEOUS ACETONE

Acetone %	Relative Solubility
0	1·0
10	0·3
20	0·15
30	0·07
40	0·04
50	0·02

A cryoscopic study of potassium fluoride in molten lithium borate as solvent has shown that the solute is completely ionized.[64] From this and other studies, lithium borate would appear to be an excellent ionizing solvent in which, for example, natural cryolite is ionized into 10 particles.

Chemical Properties

The reaction between potassium fluoride and an oxide MO (where M = Zn, Ca or Mg) leads to the formation of the double fluoride KMF_3. Of these double fluorides, $KZnF_3$ is tetragonal, having $a = 8{\cdot}49$, $c = 8{\cdot}09$; the others are monoclinic, having: $KMgF_3$, $a = b = c = 8{\cdot}00$, $\beta = 91° 18'$; $KCaF_3$, $a = b = c = 8{\cdot}80$, $\beta = 92° 36'$. All appear to exhibit various modifications of the perovskite structure.[65]

In studying the formation of complex fluorides, reactions of potassium fluoride in iodine pentafluoride, IF_5, as solvent, have been investigated.[66]

With boron trifluoride, the reaction is $BF_3 + KF \rightarrow KBF_4$, indicating the acidic nature of BF_3 in this solvent. Antimony pentafluoride, a Lewis acid, is associated with one molecule of solvent and reacts with potassium fluoride:-

$$SbIF_{10} + KF \rightarrow KSbF_6 + IF_5.$$

The system potassium–potassium fluoride has been studied. Above about 960°, the components are completely miscible. The consolute temperature is 910°. In general, miscibility of solid halides in the corresponding liquid alkali metal increases with increasing atomic weight of the metal.[67]

The reaction $NaNO_3 + KF \rightleftharpoons KNO_3 + NaF$, at 530°, takes place with $\Delta H = -8{\cdot}53$ kg.-cal./mole. In the reciprocal system of these components, shown in Fig. 1, binary eutectics are observed at 298° and 9% KF, for KNO_3–KF, and at 710° and 60% KF, for NaF–KF. The stable diagonal KNO_3–NaF divides the four-component diagram into two ternary systems. One of these, NaF–KF–KNO_3, has a triple eutectic at 295°, with composition 90·5% KNO_3, 2·5% NaF, and 7% KF. The second ternary system, NaF–$NaNO_3$–KNO_3, has a minimum point at 228°.[68]

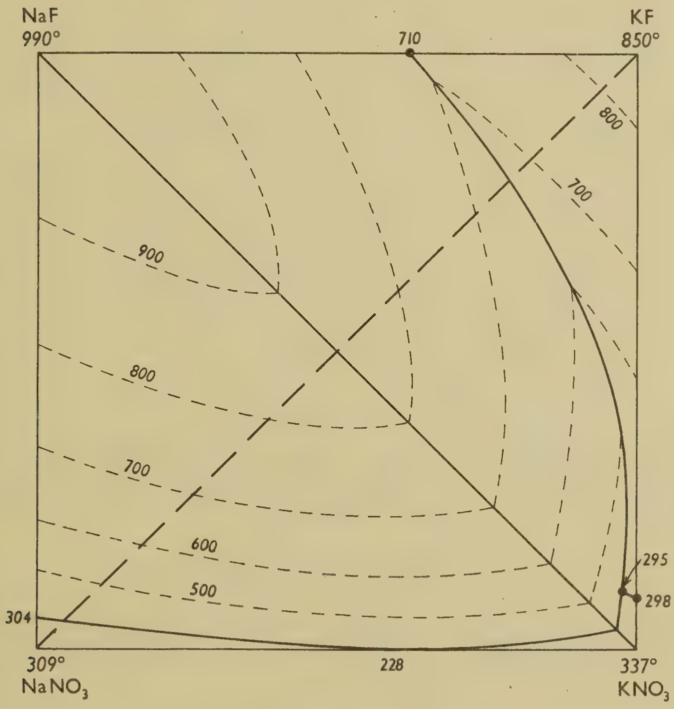

FIG. 1. THE QUATERNARY SYSTEM NaF–KF–KNO_3–$NaNO_3$

The system KF–H_2O has been investigated, and the phase diagram is shown in Fig. 2. A eutectic of ice and KF,$4H_2O$ occurs at −21·8° and 21·5 weight % KF. The compound KF,$4H_2O$,KF,$2H_2O$ melts at 18·5°.[69]

The compounds KF,4HF, and 2KF,5HF, together with the two forms of the acid fluoride KHF_2, have been found in the KF–HF system, from vapour-pressure and melting-point measurements. The above compounds exist in solutions

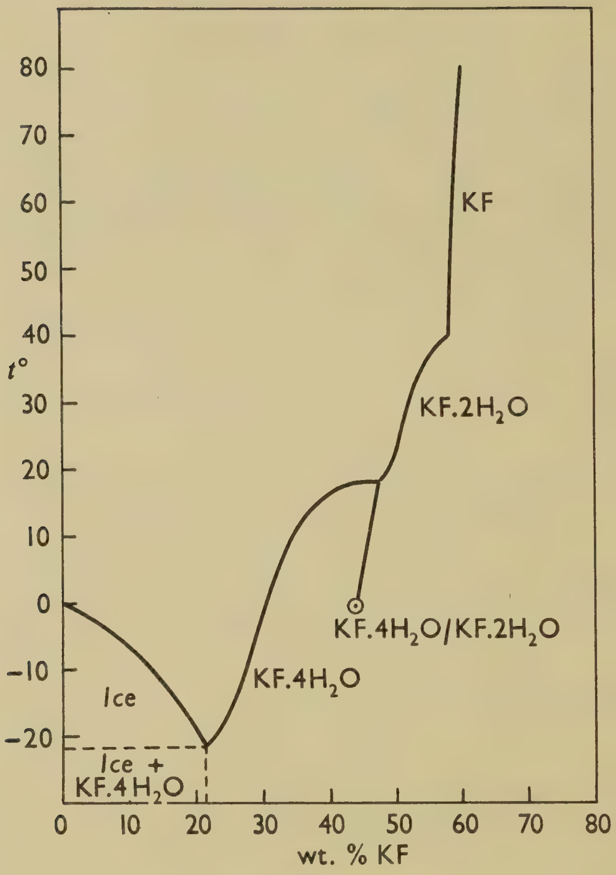

FIG. 2. THE BINARY SYSTEM KF–H_2O

containing more than 0•46 mole fraction of HF.[70] Solubility relationships at 20° have been studied for the system potassium fluoride–hydrogen fluoride–water.[71]

Phase studies of the system KF–KI–H_2O indicate a complete range of solid solutions between the two salts;[72] in the system KF–KCl–H_2O, no solid solutions or double salts are observed either at 25° or at 75°.[73]

The reaction between fused sodium and potassium and their fluorides was studied by heating the various mixtures in nickel tubes; at 1000°, the equilibrium constant for the reaction $K + NaF \rightleftharpoons Na + KF$ is 0•29 (± 0•09).[74]

The singular irreversible reciprocal system K, Ca, F, Cl has been investigated.[75] In Fig. 3, the singular points are as follows:-

a 665°, the intersection of the curves for KCl,$CaCl_2$ and CaF_2, at 19 mol.% KF.

b 968°, the intersection of the curves for CaF_2 and KF,CaF_2, at 65•8 mol.% KF.

c 592°, the eutectic of KCl,$CaCl_2$ and $CaCl_2$, at 10 mol.% KF.

d 734°, the eutectic of KF,CaF_2 and KF, at 85•5 mol.% KF.

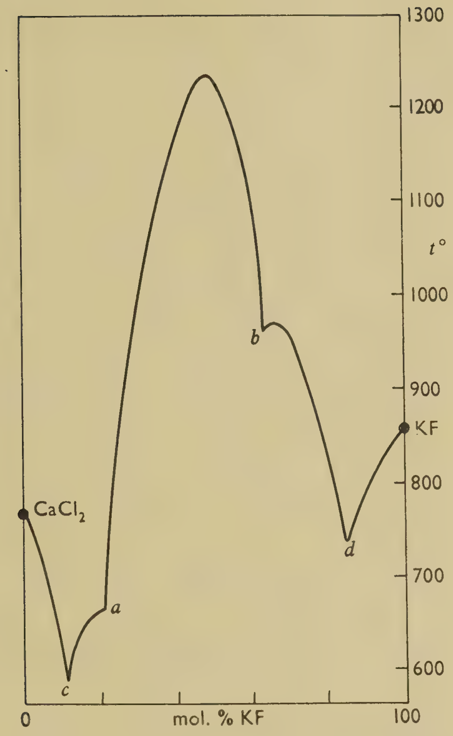

FIG. 3. THE PSEUDO-BINARY SYSTEM $CaCl_2$–KF

The compound $CaCl_2,CaF_2$ melts incongruently at 644°.
A density diagram for the binary system $CaCl_2$–KF is given in Fig. 4.

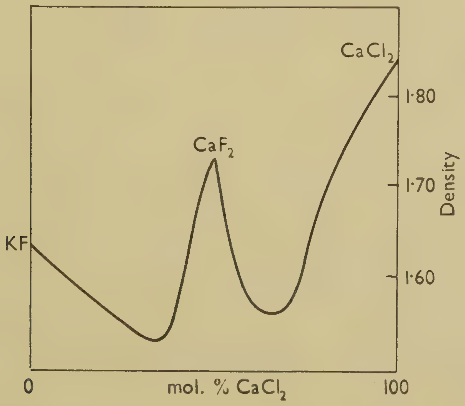

FIG. 4. THE DENSITY DIAGRAM FOR KF–$CaCl_2$ AT 1250°C.

Fig. 5 shows the behaviour of the two binary systems KF–CaF_2 and KF–KCl. The former (curve I) shows eutectic points at 782° (24 mol. CaF_2) and 1054° (70•5 mol. CaF_2), the intermediate compound being CaF_2,KF, which

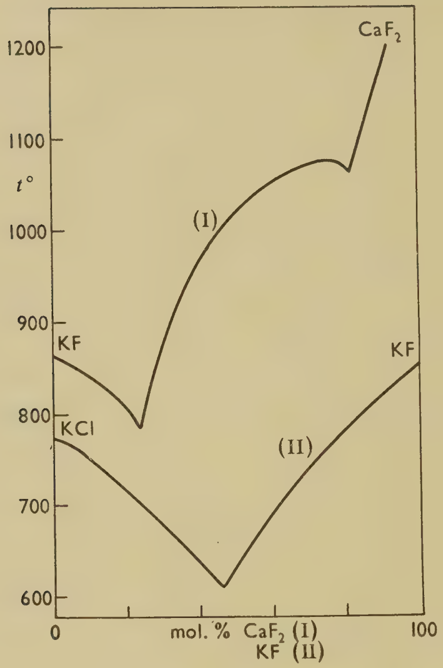

FIG. 5. THE BINARY SYSTEMS KF–CaF_2(I) AND KCl–KF(II)

melts congruently at 1070°. The latter (curve II) forms a simple eutectic mixture at 605°, 45 mol.% KF.

Fig. 6 illustrates the system CaF_2–K_2F_2–Na_2F_2.[76] Singular points are:-

a eutectic of CaF_2–Na_2F_2, at 51% Na_2F_2, 810°.

b eutectic KF–NaF, 40% NaF, 722°.

c eutectic CaF_2,K_2F_2–KF, 26·7% CaF_2, 782°.

d eutectic CaF_2,K_2F_2–CaF_2, 76·9% CaF_2, 1060°.

e ternary eutectic, at 682°, of composition 14% CaF_2, 50% K_2F_2, 36% Na_2F_2. Solid phases SI, SII and D.

p peritectic point of system CaF_2–SI–D, at 772°, and 34% CaF_2, 19% K_2F_2, 47% Na_2F_2.

Cooling curves have been plotted for the reciprocal system of fused salts: KCl + NaF $\rightleftharpoons$ NaCl + KF.[77] Five solid phases, and three series of mixed crystals, are found. In Fig. 7, the point *m* represents the KCl–NaF eutectic at 660° of this pseudo-binary system, and occurs at 28% NaF, 72% KCl. Point *e*, at 582°, represents the eutectic of the ternary system KCl–KF–NaF. Points *r* and *s*, at 605° and 722°, are the eutectics of their respective binary systems. The point *t*, at 680°, and the point *u*, 664°, are binary eutectics of the systems NaF–NaCl, and NaCl–KCl respectively; *f* is the ternary eutectic at 612°, corresponding to the composition: 50·5% KCl, 9·25% NaF.

The liquid–solid equilibria of the system:[78] $CaCl_2$–CaF_2–KCl–KF are represented in Fig. 8. The singular points of the diagram are as follows:-

a is the eutectic of $CaCl_2$ and the double salt $CaCl_2$,CaF_2 (*E*).

b is the incongruent melting-point of the compound ϕ (CaF_2,KF) at 1100°, and 30% CaF_2.

c is the eutectic of KF–ϕ, at 800°, 60% KF.

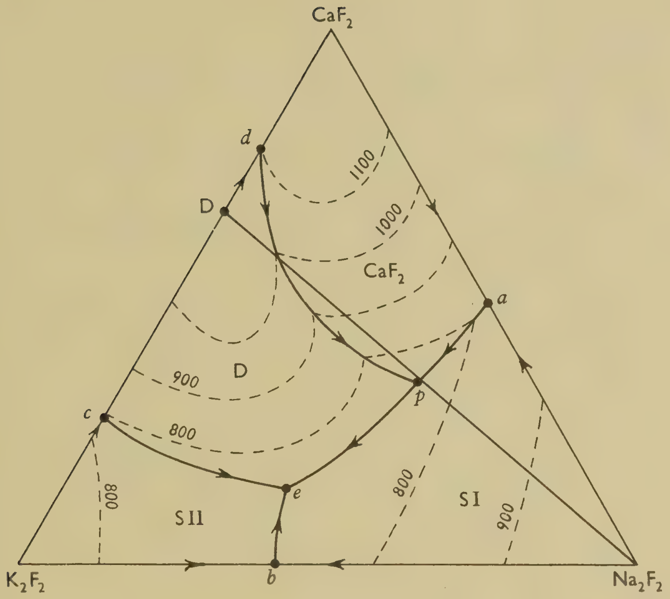

FIG. 6. THE TERNARY SYSTEM CaF_2–K_2F_2–Na_2F_2

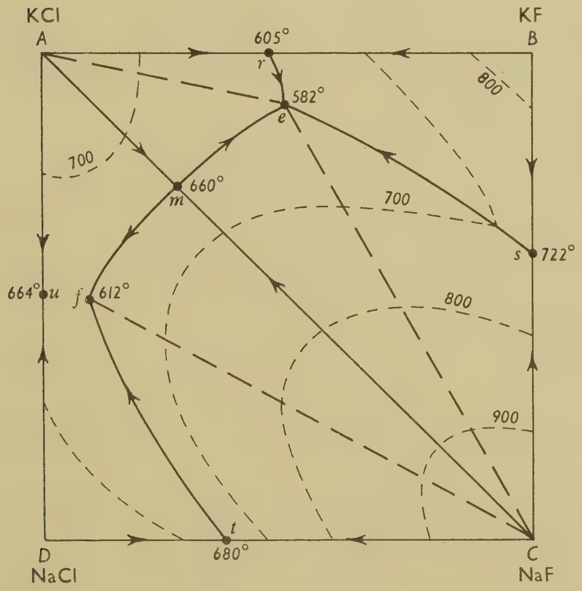

FIG. 7. THE QUATERNARY SYSTEM KCl–KF–NaF–NaCl

d is the eutectic of the binary KCl–KF system, at 605°, 45% KF.
f is the eutectic of KCl and the double salt $2KCl,3CaCl_2$ (*G*).

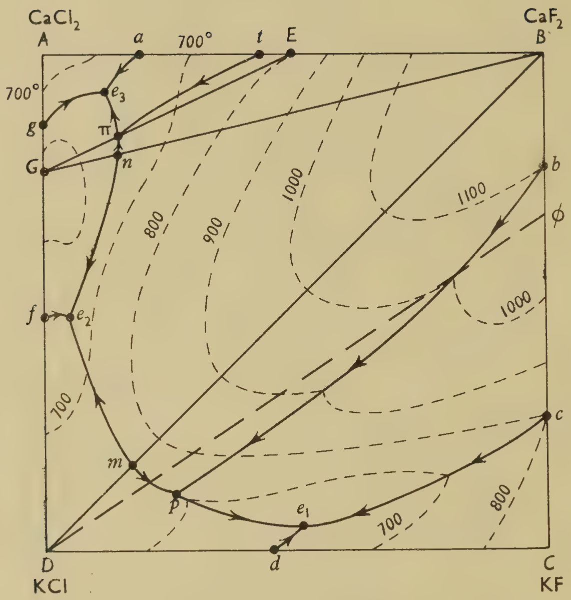

FIG. 8. THE QUATERNARY SYSTEM $CaCl_2$-CaF_2-KF-KCl

g is the eutectic of $CaCl_2$ and the double salt *G*.

t is the incongruent melting-point of the compound $CaCl_2,CaF_2$.

e_1 is the ternary eutectic, at 600°, of KCl–KF–φ with composition 49% F, 4% Ca.

e_2 is a ternary eutectic, at 582°, for the system CaF_2–KCl–$2KCl,3CaCl_2$, at 46·5% Ca, and 4·5% F.

e_3 is a ternary eutectic, at 584°, for the system $CaCl_2$–*G*–$CaCl_2,CaF_2$, *i.e.* compound *E*.

p is the peritectic point at 722°, of KCl–φ–CaF_2, 11% Ca, 25% F.

m is the maximum, at 766°, of p–e_2, and corresponds to 18% F, 18% Ca.

n is the maximum, at 663°, of e_2–π, 79% Ca, 15% F.

π is a ternary peritectic, at 656°, for the system CaF_2–*E*–*G*, at the composition 15% F, 83% Ca.

The system Na, K, || F, CO_3 has been studied;[79] the results may be expressed in terms of the four binary systems:-

NaF, Na_2CO_3: a simple eutectic point at 690° and 75% Na_2CO_3.

KF, NaF: a eutectic at 710° and 60% KF; and a limited range of solid solutions.

Na_2CO_3, K_2CO_3: a complete range of solid solutions.

KF, K_2CO_3: eutectics occur at 688° with 30% KF, and 677° with 43% KF; the intermediate compound is KF,K_2CO_3.

The salt KHF_2 behaves as a base in anhydrous hydrogen fluoride; neutralization by the acids HSO_3F, HBF_4 and $HSbF_6$, yields KSO_3F, KBF_4 and $KSbF_6$, respectively.[80] The KHF_2-water system shows a eutectic at −8° and 16% KHF_2; the diagram shows no other singularities.[81]

Analytical applications.

Potassium fluoride precipitates K_2CrF_5,H_2O from a hot solution of a chromic salt; the reaction has been studied as a possible gravimetric method for determining chromium.[82,83] Mixtures of concentrated solutions of sodium or potassium sulphate and potassium fluoride are said to form excellent substitutes for the Zimmermann–Reinhardt reagent in the analysis of iron solutions.[84] It should be remarked, however, that while the fluoride ion may be a satisfactory complexing agent for the ferric ion, a consideration of electrode potentials throws doubt on the possibility of replacing the manganous sulphate by sodium or potassium sulphate.

The following reactions are the basis of a method for the determination of the aluminium content of soils:-

$$AlCl_3 + n \text{ tartrate} + 3KOH \rightarrow Al(OH)_3(\text{tartrate})_n + 3KCl$$
$$Al(OH)_3(\text{tartrate})_n + 6KF \rightarrow K_3AlF_6 + n \text{ tartrate} + 3KOH$$

After adding the tartrate to the aluminium chloride solution, 10% potassium hydroxide solution is added until the solution is just alkaline to phenolphthalein. The solution is then neutralized with standard hydrochloric acid solution, a 30% solution of $KF,2H_2O$ added, and the liberated KOH is titrated with the standard acid, to phenolphthalein. The reaction is non-stoicheiometric, the end-point occurring approximately 10% before equivalence.[85]

Potassium bifluoride, KHF_2, has been suggested as a primary standard in quantitative fluorine chemistry and the determination of its purity has been discussed.[86] A comparative study has been made of methods available for the analysis of commercial bifluorides.[87]

Uses.

Potassium fluoride prevents efflorescence on ceramic material, such as tile.[88] It has been used as a promoter in industrial ferric oxide catalysts, for example, in hydrocarbon synthesis from carbon monoxide and hydrogen.[89,90]

Addition of 1–10% of dry, powdered potassium fluoride to uranium hexafluoride renders it stable for many months in a glass or silica container.[91]

A mixture of 1–7 moles HF with 1 mole of potassium fluoride forms a lubricant resistant to both liquid and gaseous fluorine between 0° and 300°.[92]

The electrolysis of 7% potassium fluoride in glacial acetic acid, with a platinum cathode and a silver anode, leads to the formation of pure crystalline silver fluoride. Other anodes, such as tantalum, niobium, antimony and bismuth, similarly gave the corresponding anhydrous fluorides.[93]

A mixture of 30% potassium fluoride and 70% potassium chloride forms one of a series of fluxes, suitable for aluminium welding.[94] The eutectic mixture of potassium fluoride (48%) and lithium fluoride (52%) formed at 520°, constitutes a thermosensitive resistance element.[95] A study of glasses, of the type BeF_2–LiF–MF, where M is an alkali metal, shows that the refractive index is higher for $M = K$ than for $M = Na$ or Li.[96]

Potassium fluoride is the most effective of a number of sodium and potassium salts as a salting-out agent for water–*iso*propanol, and water-*tert.*-butanol, mixtures, at 30°.[97,98]

Electrolysis of potassium fluoride in liquid hydrogen fluoride, or of molten KHF_2, yields fluorine.[99–101] In the latter case, the operating temperature may be lowered by the addition of sodium fluoride; but this is not recommended, because of the higher content of hydrogen fluoride in the evolved fluorine.

The acid fluoride, KHF_2, has been advocated as a suitable fungicide for the prevention of mould growth on leather; a 1:500 solution is effective.[102] A brazing flux for titanium, zirconium and their alloys may be prepared from KHF_2 (37·5–55%), KCl (10–37·5%) and LiF (25–35%). Potassium bifluoride, KHF_2, is used as a wood preservative and its permanence as such on storage has been considered: it is more hygroscopic than $MgSiF_6$ and loses small amounts of fluorine under conditions of high relative humidity.[104]

Refs. p. 1664

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SECTION LI

POTASSIUM CHLORIDE

By D. S. and (Mrs.) G. M. PAYNE

Occurrence, Production and Purification

Potassium chloride is widely and abundantly distributed in saline mineral deposits and in the waters of the oceans, the inland seas, and many lakes. Its occurrence in these and in minor sources of animal, vegetable and industrial origin have been fully discussed (Mellor, II, 15,428,436,522, this volume, 1460). By argon determinations, the age of the potash deposits in Buggingen and Alsace (Lower Oligocene) has been estimated as (25 + 5 or −3) × 10^6 years.[1] Potassium chloride as a source of potash is primarily of interest as a fertiliser, when it is often referred to as 'muriate of potash'. Of the salts which might reasonably serve as sources of water-soluble potassium for plant foods, potassium chloride has several advantageous features. On the basis of its equivalent K_2O content potassium chloride (63%) is more favourable than potassium sulphate (54%), phosphate or nitrate. Its extraction from the numerous mineral sources is comparatively easy, and it is becoming usual to handle material of a high grade of purity, thereby avoiding unnecessary freight charges. However, where transport is easy, material of a lower grade, containing larger amounts of sodium chloride, is often employed. Muriate of potash fertiliser is usually available in various grades, particularly as 60% K_2O (95% potassium chloride), 55% K_2O (87% potassium chloride) and 50% K_2O (79% potassium chloride). For chemical processes a higher grade (98% potassium chloride) is readily prepared by washing poorer grade crystals with limited amounts of water or dilute brine.[2]

The Section on "The Extraction of Potassium Salts from Natural Sources" (this volume p. 1459), deals largely with the production of potassium chloride, this being the commonest form of commercial potash. Reference to the extraction can also be found in Mellor, II, 526. In production from brines or solutions of mineral chlorides, the problem is essentially one of phase phenomena in multi-component systems. The high temperature coefficient of solubility of potassium chloride, compared particularly with that of sodium chloride, makes extraction comparatively easy. The flotation process has been extensively developed for the separation of potassium chloride crystals from other halides and at least fourteen patents based on this process have been granted over the past twenty years. The flotation liquid is a saturated aqueous extract of the mineral or a brine concentrate together with frothing and collecting agents, such as pine oil and a primary long chain (14–18 carbon atoms) aliphatic amine, often as the acetate. The crude mineral, crushed and finely powdered to separate the constituent salt crystal into discrete particles, is pulped with this liquid. According to conditions, potassium chloride is concentrated either in the froth,[3,4] or in the flotation liquid.[5] Lead or bismuth chloride has been added to the brine to improve the flotation separation.[4] Gravity separation is also effective in the separation of potassium and sodium chlorides.[6] The elimination of traces of lead[7] and of other impurities[8] from potassium chloride by methods amenable to industrial application has been described. The constituents of a powdered mineral may also be separated electrostatically. On agitating a hot, dry mixture of crystals of sodium and potassium chlorides, they acquire respectively positive and negative charges, and the potassium salt may then be isolated at the anodes of an electrode assembly. Application of this method to a mixture containing magnesium chloride as a third component has been investigated.[9]

Potassium chloride of a purity suitable for use in atomic weight determinations is prepared from more readily purified salts such as the nitrate,[10] chlorate,[11] perchlorate[12] or oxalate,[13] by the action of hydrogen chloride or chlorine gas under appropriate conditions. It is further purified by recrystallisation from water and dried by melting in a stream of dry nitrogen or under vacuum.[14] Pure potassium chloride containing caesium chloride 10^{-7}% and rubidium chloride 10^{-6}%, has been prepared using a cation exchange resin.[15]

Physical Properties

Potassium chloride, in particular amongst the alkali metal halides, by reason of its accessibility, purity, and convenience, has been the subject of numerous physical investigations. In many cases its function has been merely that of a convenient uni-univalent electrolyte and except in special cases reference to this type of investigation is omitted from the account which follows. Only material pertaining directly to potassium chloride is discussed.

Solid State.

Potassium chloride was shown by Bragg in 1914[16] to have a 'simple cubic' structure, with the space group O_h^5 $(Fm3m)$. The unit cell contains 4 'molecules'.[17] The side of the unit cell, a, has been variously reported as 6·276 ± 0·006,[18] 6·280 ± 0·003,[19] 6·277 ± 0·002,[20] 6·293,[21] 6·26,[22] or 6·272 A.[23] The most recent values are summarised in Table I[24]

TABLE I.- UNIT CELL, DIMENSIONS FOR POTASSIUM CHLORIDE IN A. AT 25°C.

	a
Tu[25]	6·29229
Batuecas and Fernandez-Alonso[26]	6·307
Hutchinson[27]	6·30511
Vegard[28]	6·289
Swanson and Tatge[24]	6·2931

The values of Hutchinson and Batuecas and Fernandez-Alonso are from precision density determinations, not X-ray measurements. Precision measurements of the lattice constant at 25°C. of a spectroscopically pure specimen gave a value of 6·2929 ± 0·00008 A., with a coefficient of linear expansion (15°C.–25°C.) of $3{\cdot}3_7 \times 10^{-5}$/°C.[29], and independently with a very pure specimen, 6·292 A. and a coefficient of linear expansion (25°C.–100°C.) of $3{\cdot}8 \times 10^{-5}$/°C.[30] Densities of pure and calcium-containing single crystals of potassium chloride, determined directly, are in good agreement with densities calculated from precision X-ray data. Equations are given for the temperature dependence of the lattice constant and the coefficient of linear expansion of potassium chloride between 20°C. and 600°C.[31]

In Laue photographs of potassium chloride crystals taken perpendicular to the [100] plane, radial lines are observed.[32] These have been variously interpreted as due to a two-dimensional lattice[33] and to imperfections.[34] The diffuse nature of Laue spot photographs due to thermal vibrations[35] has been the subject of theoretical investigation into the relation between thermal scattering of X-rays and the elastic constants of the lattice.[36]

X-Ray measurements show that grinding a powdered sample of potassium chloride produces very little, if any, lattice distortion.[37] The ratio of the intensities of the *X*-ray reflexion from the [200] and [400] planes increases under compression.[38] It is reported that the lattice constant of a sample of potassium chloride just after formation by evaporation is greater than the accepted value by about 0·15%. On exposure to air or on annealing, the lattice constant decreases, but no explanation is given other than the possibility of the presence of impurities or imperfections.[39]

The scattering of *X*-rays from the powdered crystals has been investigated.[40] Using Mo K_α radiation, the effect is approximately the same as from gaseous argon.[41]

The lattice constant, $a = 6\cdot286_5 \pm 0\cdot0007$ A., of a potassium chloride film determined by electron diffraction using gold foil as a standard is 0·3 to 0·15% larger than the *X*-ray values,[42] (see above[39]). However, very precise electron diffraction measurements of the lattice constant have shown that there is no variation in spacing as compared with *X*-ray measurements, with small crystallites down to 150 A. For crystal sizes less than 100 A. the lattice constant was, in fact, found to be less than the *X*-ray values by an amount dependent on crystal size; for a crystal of about 50 A., the decrease was approximately 0·5%.[43] A lattice constant of 6·22 A, is reported from an electron diffraction study.[44] It should be noted that specimens of potassium chloride suffer destruction under the action of an electron beam,[45] as for example, in the electron microscope. A distinct specular beam is produced by the action of a beam of cadmium atoms striking a crystal of potassium chloride.[46] Neutron diffraction with potassium chloride single crystals gives structure factors in close agreement with those obtained by other methods.[47] Determinations of the crystal structure of potassium chloride have been reviewed.[48]

The calculated density from *X*-ray measurements is 1·9865 at 25°C.,[24] 1·9897 ± 0·0001 at 18°C.,[49] and 1·9901 ± 0·00015 at 15°C.[50] The density of potassium chloride is reported to be independent of particle size over a range of average diameters of 0·1–5·0 mm. and to have a value of 1·9891 at 25°C.[51,52] Recent precision measurements of density have given the values $d_4^0 = 1\cdot9917 \pm 0\cdot003$,[26] and 1·98721 ± 0·00002 g./ml. at 25°C.[27] For the latter result, six precipitations of the potassium chloride were required before constancy was obtained and a surface effect amounting to a change in density of 10^{-4} g./ml. occurred on standing in the atmosphere for two hours; storage over phosphorus pentoxide under vacuum eliminated this effect. The density has also been quoted as 1·9905 g./ml. at 16·00°C.,[52] and the specific gravity as 1·983 at 20°C.[53] The shrinkage of powdered potassium chloride on fritting has been investigated by an *X*-ray method.[54]

Details of the growth of potassium chloride crystals and the circumstances of the production of various crystal habits are given later. (see page 1682)

The heat capacity, (C_p), of potassium chloride has been measured over various ranges of temperature, *viz.* up to its m.p.,[55] 20°C.–40°C.,[56] 83°–298°K.,[57] 15°–290°K.,[58] 12°–300°K.,[59] 10°–273°K.,[60] 2·3°–17°K.,[61] <4·0°K.,[62] 1·5°–4·0°K.[63] At 1·5, 2·0, 2·5, 3·0, 3·5, and 4·0°K., the specific heats are 1·00, 2·34, 4·66, 8·13, 13·1, and 19·7 × 10^{-3} *J*/mole°C., respectively.[62] The mean heat capacity in the range 20°–400°C., C_p, is $0\cdot1612 + 3\cdot21 \times 10^{-5}t$ g.-cal./g.[56] The calculated values for the specific heat of potassium chloride at low temperatures are in agreement with experiment.[64] The standard entropy for solid potassium chloride, S_{298}, is 19·76 ± 0·1,[65] 19·75 ± 0·06,[58] 19·68 ± 0·05,[59] 19·35 ± 0·5 g.-cal./mole°C.[66] The free energy of formation for the reaction 2K (solid/liquid) + Cl_2 (gas) → 2KCl (solid), is given by the expression:

$$\Delta G_{298-1043^\circ\mathrm{K.}} = -209{,}800 + 48{\cdot}0\,T$$[67]

The constants in the vapour pressure equation, $\log_{10}p = -(A/T) + B$, are shown in Table II.

TABLE II.- CONSTANTS IN THE VAPOUR PRESSURE EQUATION $\mathrm{LOG}_{10}p = -(A/T) + B$ FOR POTASSIUM CHLORIDE

Units of p	A	B	Range°K.	Reference
mm. Hg	11070	10·151	855—1024	68
mm. Hg	11310	10·451	711—870	69
dynes	11300	13·461	847—936	70
mm. Hg	11300	10·336	847—936	70

Other data have been fitted to the equations

$$\log_{10}p_{\mathrm{mm.}} = -12229/T - 3\log_{10}(T/1000) + 11{\cdot}341$$[71]

$$\text{and } \log_{10}p_{\mathrm{mm.}} = -11{,}879/T - 2\log_{10}(1000/T) + 11{\cdot}006.$$[66]

The respective heats of sublimation over the ranges quoted in Table II are 50·2[68] and 51·8 kg.-cal./mole,[70] whilst values of the heat of vaporisation calculated to 0°K. are 54·43 ± 0·5[69] and 52·0 ± 0·9 kg.-cal./mole.[72] The volatility of potassium chloride at high temperatures in streams of air, water vapour, ammonia, and hydrogen chloride has been determined.[73]

The thermal conductivity of potassium chloride shows a maximum at 10°K.[74] At 81·8°, 14·62°, 4·28° and 1·92°K., the corresponding values are 2·73, 0·490, 0·360, and 1·67 w^{-1}.[75] The thermal conductivity of the salt at temperatures between 2° and 5°K. has been discussed on theoretical grounds.[76-78]

The dielectric constants of powdered and crystalline potassium chloride in vacuo or in air,[79-85] and in certain binary mixtures of mutually soluble liquids in which the salt is inert and insoluble,[86-89] have been investigated. For dispersions in benzene and nitrobenzene,[86] and in toluene and chlorobenzene,[87] the proportions of the respective components of the mixtures may be so adjusted that when the system exhibits dielectric homogeneity, the value of the dielectric constant may be deduced directly from that of the liquid phase. Values of 4·74 and 4·73, respectively, have been obtained. The dielectric constant of powdered potassium chloride measured in air or in vacuo is 4·68 ± 0·01 at 20°C., λ = 100 m.,[88] 4·54 at 19°C., λ = 1800 m.,[83] 4·76;[90] in benzene, 4·94 at 19°C., λ = *ca.* 350 m.;[91] in chlorobenzene, 4·80 at 80°C.; and in chloroform, 4·64 at 29·5°C., λ = 310 m.[92] A linear relationship exists over a limited range between the bulk density of powdered potassium chloride and its dielectric constant.[83] The relationship between the dielectric constants of powdered and crystalline potassium chloride has been discussed.[80-82] The dielectric constant of potassium chloride as calculated from that of the powdered salt is 5·13.[85] The effect of increasing the pressure is to decrease the dielectric constant. Measurements made over a pressure range 0 to 8000 bar at 1000 c.p.s. and at room temperature, show $(\partial \ln \epsilon/\partial p)_T = -1{\cdot}05 \pm 0{\cdot}08 \times 10^{-5}$/bar.[93] A theoretical study of this phenomenon has been made.[94] Abnormal values of the constant and of the loss angle in the region of 3 Mc./sec. have been studied.[95] Dielectric breakdown in single crystals of the pure salt[96-105] has been discussed in the light of theories concerned with the abundance, in the crystals, of electrons at various energy levels, and with other processes. The dielectric strength can be expressed in terms of static and optical dielectric constants and the energy of the optical frequency of lattice vibration.[104] The effects of temperature and of potentials producing direct, alternating, or pulsed breakdown currents[97] have been treated in semi-quantititive terms. The ease, hitherto unsuspected, with which crystals of pure potassium chloride acquire structural defects through plastic deformation, and the effect of such dislocations on dielectric strength, have prompted the view that values of this property for the alkali metal halides, as published prior to 1953, may be as much as 50% too high.[101] It is probable that a trustworthy value is 1·1MV./cm., since this, obtained in 1954, fits smoothly into an orderly gradation of values obtained for eleven other alkali metal halides.[102] This value is in fair agreement with those of 1·25 and 1·0Mv/cm. obtained by A. von Hippel in the case of natural and prepared crystals, respectively.[103] Electron avalanche distributions have been studied for temperatures between 55°C. and 210°C. At the lower end of this range, breakdown is initiated by a relatively small number of high-energy electrons, whilst towards the upper end, electrons of lower energy occur in such abundance as to exercise predominance of control.[99,100]

The electrical conductivity of potassium chloride as single crystals,[106-110] of thin films deposited by vacuum evaporation,[111] of pellets prepared by plastic deformation,[107,109,112] and of powders obtained by grinding the salt in vacuo and in air,[113] has been investigated at different temperatures,[106,108,114] potential gradients,[108,114] and humidities,[113] and the results discussed in terms of various theories relating to electronic processes in ionic crystals. Between −180°C. and the melting point, the conductivity and its temperature coefficient follow Ohm's law and the van't Hoff equation, respectively, but with high potential gradients the conductivity increases with field strength.[115,116] For flat crystal plates of the salt under potential stresses of 0·05 to 0·09 KV./cm., the specific conductivity rises exponentially with temperature from 10^{-17} mhos at 25°C. to about 10^{-6} at 600°C., with an abrupt rate of increase in the 200°–250°C. range. At room temperatures the current decays exponentially with time, but towards 600°C. it remains almost constant.[108] The conductivity of the salt on heating passes through a maximum, then a minimum, and then rises exponentially, becoming large at 420°C. On re-heating, the maximum disappears almost completely. The relation between current, i, and the voltage, V, at low temperatures is given by the equation $i = kV^{3/2}$, k being a constant. At high temperatures the relation is linear.[114] The heats of liberation for crystal and pellet forms of the salt, as calculated from temperature-conductivity measurements, are $32{\cdot}1 \times 10^{-13}$ and $30{\cdot}3 \times 10^{-13}$ ergs per ion, respectively, at high temperatures. Corresponding values at lower temperatures are about 50% lower, namely, 15×10^{-13} and $14{\cdot}7 \times 10^{-13}$; thus, both ions contribute to conductivity at high temperatures, whilst as the temperature is decreased only the positive ion is involved.[107] Supporting this observation is the fact that the transport numbers at 435°C. and 600°C. are, for the anion, 0·081 and 0·044, and for the cation, 0·956 and 0·883, respectively.[117] The statement that the specific conductivity of pellets of the salt exceeds that for the crystal is open to question, since the errors in the investigation were ± 8%.[109] The increase in conductivity of potassium chloride observed during plastic deformation is attributed to the liberation of electrons in the vicinity of slip planes in the crystal.[112] Anomalies in conductivity and dielectric data for the powdered salt, as prepared by grinding, are caused by adsorption of atmospheric moisture.[113] Films of potassium chloride deposited by vacuum evaporation undergo crystalline transformation after heat treatment, whereupon the conductivity decreases to a value between 0·1 and 0·01 times that observed for freshly prepared specimens.[111] As part of a general study of ionic crystal dielectrics, the relation between conductivtiy and dielectric loss at 650Mc./sec. has been studied for potassium chloride. An increase in temperature from about 20° to 220°C. results in a several hundredfold increase in conductivity, but no significant change in the value of $\tan^{-1} 0{\cdot}0027$ is observed for the dielectric loss angle. On the basis of these phenomena, the suggestion has been made that in homogeneous dielectrics of simple lattice structure, as typified by potassium chloride, those electrons that are nearly free determine the dielectric loss, whilst electrical conductivity, on the other hand, depends on those that are nearly bound.[118] Exposure to sunlight does not affect the conductivity of the potassium chloride crystal, and the effect of *X*-rays alone is but slight. The combined effect, however, especially for ultra-violet radiation, is to cause a 40,000-fold increase in conductivity.[119]

The self diffusion of potassium[120] and sodium[121] ions in potassium chloride single crystals has been measured using radioactive isotopes. The mobilities of copper and gold ions are greater in crystals of potassium chloride than in sodium chloride. In potassium chloride the ionic mobility (μ), of the copper$^{\text{II}}$ ions is greater than that of the gold$^{\text{III}}$ ions. ($\log_e \mu_{\text{Au}} = \log_e 133{\cdot}6 - 15{,}000/T$, $\log_e \mu_{\text{Cu}} = \log_e 645 - 15{,}200/T$).[121a]

At 18°C. and 25°C. the refractive indices of crystalline potassium chloride are 1·4904 and 1·4897, respectively, and the molecular refractivity at the latter temperature is 10·83.[122] The reflexion of electron beams from potassium chloride surfaces has been investigated.[123] The reflecting power for electrons of the face of a potassium chloride crystal is at a minimum for electron energies which correspond to the limits of optical transparency.[124] Transmission curves for potassium chloride heat-treated at 100°, 200°, and 750°C., and containing 0·01% of lead chloride, are reported.[125] Potassium chloride crystals exhibit double refraction when stressed.[126]

The effects of time and pressure on the plastic flow of single crystals and of a crystalline aggregate have been followed by optical and *X*-ray measurements.[127] A study of the flow of potassium chloride under pressure at 5°–80°C. has revealed that phase conversion takes place at about 20°–25°C. At 5°C., conversions also occur at pressures of 3700 and 6460 kg./sq.cm., respectively, these phenomena having been confirmed by measurements of the coefficient of compressibility and relaxation of stress. The curves of pressure versus flow, as obtained in this investigation, differ, however, from those reported by earlier workers.[128] The use of discs of potassium chloride and of other alkali metal halide crystals as observation windows in high pressure apparatus has been discussed from the viewpoint of the elastic properties and strengths of these substances.[129] Third order elastic constants for various substances crystallizing in cubic form, including potassium chloride, have been calculated.[130] The potassium chloride lattice is reported to undergo no change in structure at pressures up to 14,000 kg./sq.cm.,[131] but experiments up to 50,000 kg./sq.cm. suggest that the salt assumes the cæsium chloride type of configuration at 20,000 kg./sq.cm.[132] Values for the elastic properties of the salt, as derived on theoretical grounds, are in fair agreement with those obtained experimentally.[133,134] The principal adiabatic and isothermal elastic constants of potassium chloride have been determined from 80° to 280°K.,[135] and at other temperatures,[136] and the variation of compressibility with temperature and pressure has been studied at 30°C. and 75°C. up to 12,000 kg./sq. cm.[137] A vibration method has been employed for determining the hardness of the crystal,[138] and an expression derived whereby the compressibility of the crystal has been correlated with the absorption frequency.[139] The elastic properties of polycrystalline aggregates of potassium chloride formed by compression of the powdered substance at 60,000 lb./sq.in. have been compared with those of the monocrystalline variety.[140] The modulus of compression has been calculated from the polarisation coefficient for a static and an alternating field.[141,142] The average internal pressure in potassium chloride is calculated as 65,000 kg./sq.cm.[143] The resistance of powdered potassium chloride to compression by both static and impact loads, is described.[144] Because the ratio of Young's modulus in the [100] to [111] planes is very much greater than that for sodium chloride, potassium chloride is a convenient substance for the study of gliding mechanism in crystals.[145]

The heat of wetting of powdered potassium chloride by carbon tetrachloride is 0·055 g.-cal./g. for a sample passing a sieve 900 mesh/sq. cm.; for a finer powder passing a sieve 3600 mesh/sq. cm. the value is 0·063 g.-cal./g.[146] The ratio of the surface energies of two crystals can be calculated from measurements of the amount of material abraded, when, for example, silicon carbide, as an abrasive powder, is placed between the [100] faces of the two crystals and they are then moved relatively to one another.

Data for potassium chloride with other alkali halides are in agreement with surface energy data obtained from other sources.[147] The adsorption of argon, krypton, and carbon dioxide by finely powdered potassium chloride has been measured at various temperatures and the heats of adsorption are calculated as 1900, 2400, and 6200 g.-cal., respectively.[149] The adsorption of argon and nitrogen at −195·8°C. and −183°C.; of carbon dioxide and oxygen at −183°C.; of carbon dioxide at −78°C.; and of *n*-butane and sulphur dioxide at 0°C., on powdered crystals of the salt has been measured.[150] Argon, at −188·5°C. to −185°C., does not absorb as thick films onto the surface of potassium chloride.[151] Adsorption of argon on the [111] plane of octahedral crystals, in which there exist two different arrays of ions, has been investigated.[152,153] Theoretically predicted differences between adsorption of the gas on the [100] and [111] planes have been confirmed experimentally.[153] It appears by comparison with other published data that about 80% of the surface of a sample of powdered potassium chloride studied was composed of [100] faces.[154] Adsorption isotherms at −183°C. for ethane on potassium chloride show first order phase changes at pressures of 4–5 × 10^{-6} mm.Hg.[155] The heat of adsorption of argon, oxygen, and nitrogen on potassium chloride crystals at 69°–87°K. is 1860, 1750, and 1400 g.-cal./mole, respectively.[156] The energy of adsorption can be calculated successfully for nitrogen molecules which are regarded as having an electrical quadruple interaction with the surface of the crystal.[157] The adsorption of air by previously heated specimens of the salt has been studied.[158]

The molar diamagnetic susceptibility of potassium chloride is $-39{\cdot}1 \times 10^{-6}$;[159] $-38{\cdot}8 \times 10^{-6}$ at 20·2°C.;[160] $36{\cdot}15 \pm 0{\cdot}36 \times 10^{-6}$;[161] $-35{\cdot}8 \times 10^{-6}$;[162] $-39{\cdot}0 \pm 0{\cdot}5 \times 10^{-6}$.[163]

The occurrence of coloured crystals of the alkali halides in nature is well known. This is one aspect of the phosphorescence of alkali halide crystals which has been the subject of much investigation, particularly within the past twenty years. There have been many notable contributions to knowledge in this field, which is expanding rapidly. It has been well reviewed by F. Seitz in two papers, one in 1946[164] the other in 1954.[165] Interest in these particular phosphors centres largely on their very great utility in apparatus for the detection and measurement of radiation. The coloration is associated with colour centres (so-called "F" centres) which arise from an excess of alkali metal in the crystal lattice, this being equivalent to free electrons in the lattice. This type of lattice defect can be produced by *X*-rays,[166] γ rays,[166] or electrons[167] impinging on the crystal, or by direct incorporation of alkali metal.[168] (see also page 2526).

For potassium chloride, a large amount of information exists, much of it referring to crystals containing a small amount of an 'impurity'. Thallium is a particularly favourable 'impurity', producing when ~1% is present a crystal which can be excited by ultra-violet light to give an intense ultra-violet and blue emission having a long period of duration. Other heavy metal ions, such as lead or copper, show similar effects. Potassium chloride which has been ground finely is more rapidly coloured by *X*-rays than precipitated potassium chloride.[37] The number of defects (colour centres) in a pure crystal of potassium chloride can be as great as 10^{17} per c.c. A density difference between coloured and pure crystalline potassium chloride is detectable.[169] The magnetic susceptibility of the colour centres is temperature-independent at room temperature and temperature-dependent at the temperature of liquid helium.[170] Paramagnetic resonance absorption is observed at room temp. at $9\cdot0 \times 10^{9}$ c./sec. in potassium chloride containing an excess of potassium.[171] Electronic photoconduction is associated with the existence of "F centres" in the crystals.[172,106] The mobility of the electron centres has been treated theoretically and also measured experimentally.[173] The thermal conductivity of crystals of potassium chloride containing 5×10^{18} colour centres per c.c. is less, by a few %, than that of a pure single crystal.[174] The dielectric properties of coloured crystals are reported.[105]

Centres can be destroyed by raising the temperature of the crystals,[175] or by irradiation with polarised light.[176]

Liquid State.

The melting point of potassium chloride has been taken as a standard temperature (770·3 ± 0·5°C.).[177] The density over the range 800 – 880°C. is given by the expression $\rho = 1\cdot535 - 0\cdot00056\,(t - 768)$ g./c.c.[178] The electrical conductivity of molten potassium chloride, (cf. Mellor, II, 550), has been re-measured as 2·65 ohm^{-1} cm.$^{-1}$ at 1000°C.;[179] at 800°C., 2·19; at 850°C., 2·30; at 900°C., 2·40; and at 930°C., 2·47 ohm^{-1} cm.$^{-1}$ [180] The activation energy for conduction is 3·32 kg.-cal./mole.[179]

Data on the electrode potential of various metals in molten potassium chloride have been collected and reviewed.[181] The decomposition potential of molten potassium chloride, using carbon electrodes, is 3·22 V. at 800°C. and 3·00 V. at 925°C.[182] A distinction has been drawn between the decomposition potential of 2·8 V. at 800°C.[184] and the equilibrium reaction potential of 3·37 V. at 800°C.[185] During the electrolysis with carbon electrodes, under certain conditions a disturbance occurs at the anode when the electrolyte appears not to wet it, and a sudden drop in current density occurs. This is referred to as the 'anode effect'.[186,187]

The vapour pressure of molten potassium chloride over the range 906°–1105°C. is given by the equation:

$$\log p_{\text{mm.}} = -9115/T + 8\cdot3526 \quad [188]$$
$$\text{or } \log p_{\text{atm.}} = -40{,}500/4\cdot57T + 5\cdot2493 \quad [189]$$

The vapour pressure at 801°C. is reported as 1·54 mm.; at 948°C., 8·33 mm.; at 1044°C., 24·1 mm.; and at 1500°C., 760 mm.[190] The latent heat of vaporisation is 41·66,[188] 38·49,[189] 30·8[190] kg.-cal./mole. The boiling point at atmospheric pressure is 1411°C.[191]

Melt Systems of Potassium Chloride.

Since the publication of Mellor, II, information has been published on many systems of potassium chloride with other compounds (excluding aqueous systems) as indicated in the following Tables III, IV, V, VI, VII, and VIII and in the accompanying text.

Sodium chloride forms a continuous series of solid solutions with potassium chloride, unstable below 500°C. The freezing point minimum has been variously given as 650°C.,[205] 658°C., [206] and 661°C.[194] At this minimum, the components are present in equimolecular proportions,[194,206] or nearly so.[205] Homogeneity of the solid solutions has been demonstrated by the fact that while crystals of sodium and potassium chlorides are coloured yellow and reddish-violet, respectively, by exposure to cathode rays, the colour of the mixed crystals is uniformly intermediate between those of the component salts.[207] Solid solution single crystals of the two salts break up into their components on exposure to air, or on heating between 170°C. and 430°C. The lattices of the

TABLE III.- BINARY SYSTEMS CONTAINING POTASSIUM CHLORIDE (ALL COMPOSITIONS REFER TO MOLE% POTASSIUM CHLORIDE UNLESS OTHERWISE INDICATED)

System	Remarks	Reference
KCl–LiCl	Liquidus and solidus curves over whole range	192
	Eutectic at 352°C., 43 mole%	193
	Eutectic at 361°C., 58 mole%	194
	Eutectic at 354°C., 41·7 mole%	195
	Electrical conductivity 290°–350°C.	196
	Electrical conductivity and molar volume	197
	Electrical conductivity and coefficient of internal friction	198
	Surface tension in air 118 dynes/cm. at 427°C., interfacial tension with bismuth metal over range 370°–480°C., 240 dynes/cm. and independent of temperature	199
	Polarography with platinum microelectrodes	200
KCl–LiOH	Phase diagram	193
KCl–$LiNO_3$	Cryoscopic study	201
KCl–NaF	Eutectic at 653°C., 81 mole%	202
	Eutectic at 582°C., 5 solid phases and 3 series of mixed crystals recognised from cooling curve data	203
	Eutectic at 630°C., 82 mole%	204
	Activities of components derived from phase diagram	204*a*
	Establishment of equilibrium, *X*-ray powder patterns	204*b*

resulting crystallites are oriented parallel to the original crystal lattice.[208, 209] The kinetics of segregation in solid solution of sodium and potassium chlorides has been followed by optical measurements, the activation energy for thermal rearrangements between the potassium and sodium ions being 22·0 kg.-cal./mole.[210] The heat evolved in the 'ageing' of KCl–NaCl solid solutions has been measured directly, values varying from 920 to 1070 g.-cal./mole. The decomposition has been studied in relation to the thermal history of the samples. Simultaneously active relaxation and nucleation processes appear to characterise the breakdown.[211] A bibliography of 76 references is available.[211] The heat of formation of the solid solution has been calculated.[212, 213] The homogeneous solid solution is also reported to decompose into two partially miscible solutions with an upper consolute temperature of 490 ± 5°C. at 33 mole% of potassium chloride. The experimental molar heat of formation is given in terms of the mole fraction.[214] Recent precision calorimetry has given the heats of formation at 25°C. in g.-cal./mole as 402 ± 2, 858 ± 2, 1046 ± 6, 877 ± 2, and 464 ± 3, for 0·900, 0·700, 0·500, 0·300, and 0·100 mole% respectively of potassium chloride. The data have been extended to measurements of densities and lattice spacings and the percentage of Schottky defects is calculated as 0·09, 0·49, 0·82, 1·14, and 0·20, respectively.[215] The vapour pressure at 1180°C., of a molten mixture of potassium and sodium chlorides, has been measured.[216] The mixture behaves as an ideal solution, obeying Raoult's Law.[217] The specific conductivity of a melt containing potassium and sodium chlorides has been measured.[218] In a molten equimolecular mixture of potassium and sodium chlorides at 700°C., the discharge potentials of the following ions are in the order: hydroxide, nitrate, sulphide, sulphate, chloride.[219] The dielectric loss angle for potassium chloride containing 8% and 50% of sodium chloride has been measured at 3 Mc.[220] The growth of large single crystals is described.[221] The equilibrium between potassium and sodium metals alone and in the form of lead alloys, with mixtures of potassium and sodium chlorides at 800°C. and 900°C. has been studied. For a given mixture, the ratio of sodium to potassium in the solid phase was found to be constant. The equilibrium in the fused salt follows the law of mass action.[222] The magnetic susceptibilities of mixtures of potassium and sodium chlorides pass through a maximum at 50 mole%.[222a]

TABLE IV.-BINARY SYSTEMS CONTAINING POTASSIUM CHLORIDE (CONTINUED) (ALL COMPOSITIONS REFER TO MOLE% POTASSIUM CHLORIDE UNLESS OTHERWISE INDICATED)

System	Remarks	Reference
KCl–NaBr	Vapour pressure of system over a limited range of temperature	217
	Equilibrium constant = 1·75 at 769°C.	223
	Establishment of equilibrium below m.p. of solids. *X*-ray powder pattern reported	204 *b*
KCl–NaI	Eqilibrium constant = 1·62 at 777°C.	223
	One triple eutectic at 504°C., 16·5 mole%, KI 46·5 mole%, NaCl 37 mole%	224
	Electrical conductivity and densities, the phase diagram indicates the existence of intermediate phases	225
	Vapour pressure of system	226
KCl–$NaNO_3$	Establishment of equilibrium	204 *b*
KCl–Na_2SO_4	Phase diagram	206
	Cryoscopic study	227
KCl–Na tungstate	Phase diagram	228
KCl–KF	Eutectic at 606°C. and 55 mole%	229

In the isomorphous binary system KCl–KBr, the melting point curves resemble Roozeboom's curves for the aqueous distribution of the two salts,[230] and it has been shown from a study of the approximate phase diagram, as determined theoretically, that a gap in miscibility occurs at room temperature.[231] The heat of formation of annealed 50 mole% potassium chloride crystals diminishes slowly with time, from a maximum value of 263 g.-cal./mole, to 231–234 g.-cal./mole in six to ten months.[232] Annealing for 120 hr. at 680°C. produces a specimen with the high heat of formation.[233] This variation of heat of formation has been thoroughly studied both experimentally and theoretically.[234-241] Vapour pressure measurements at 1250°C. show the molten mixtures to be ideal solutions obeying Raoult's Law.[217] Other data based, however, on only four compositions at 590°C., show deviations from Raoult's Law.[242] *X*-Ray diagrams of the solid solution show that Vegard's Additivity Law holds within experimental error.[243-245] Potassium chloride and bromide rubbed together show by the broadening of the *X*-ray powder lines that mixed crystals have been formed.[246] The ionic conductivity shows a maximum at 30 mole% of potassium chloride for a constant temperature, corresponding with a minimum in the melting point curve.[247] The dielectric breakdown of mixed crystals of potassium chloride and bromide has been considered theoretically and compared with experimental data.[248] The surface tension of this system has been reported.[249] The magnetic susceptibility of mixtures of potassium chloride and bromide passes through a maximum at 70 mole%.[222a]

With rubidium chloride, potassium chloride yields a continuous series of

TABLE V.-BINARY SYSTEMS CONTAINING POTASSIUM CHLORIDE (CONTINUED) (ALL COMPOSITIONS REFER TO MOLE% POTASSIUM CHLORIDE UNLESS OTHERWISE INDICATED)

System	Remarks	Reference
KCl–KI	Melting point diagram	224
	Partial pressures and activities of the single components determined	216
KCl–KOH	Two incongruently melting compounds, 2KOH,KCl and KOH,KCl	193
$KCl-KNO_3$	Deviations from ideality explained by solvation	250
$KCl-K_2SO_4$	Eutectic, 690°C. and 58 mole%	206
KCl–KCNS	Eutectic, 170·2°C., 2·45 by weight% KCl	251
KCl–KCNS	Suggestion of existence of metastable eutectic	252

mixed crystals, both from the liquidus state[253,254] and by crystallisation from aqueous solution.[255] A melting point minimum is observed at 715°C. with 40 mole% potassium chloride.[253] The densities of the mixed crystals are recorded.[254] The heats of formation of KCl–RbCl solid solutions have been calculated,[235,238,241] and shown to compare satisfactorily with the experimentally determined value of 203 g.-cal./mole (50 mole% of potassium chloride).[255] The dielectric breakdown of mixed crystals of potassium and rubidium chlorides has been considered theoretically and compared with experimental data.[248]

TABLE VI.-BINARY SYSTEMS CONTAINING POTASSIUM CHLORIDE (CONTINUED)

System	Remarks	Reference
KCl–RbBr	Refractive index study of system	256
	Refractive index measurements show only one solid solution present	257
	Reaction of KCl and RbBr at 400°–600°C.	258
$KCl-NH_4Cl$	*X*-Ray powder photographs of mixed crystals studied by thermal decomposition	244
	Disperse nature of mixed crystals studied by thermal decomposition	259
$KCl-NH_4NO_3$	Phase diagram	260
	Phase diagram	261

The effect of adding relatively small amounts of alkaline earth ions to potassium chloride crystals has been studied experimentally[262] and theoretically.[263] The bivalent ions remain dispersed throughout the potassium chloride when the crystal is quenched to room temperature from elevated temperatures. The ions are not mobile until about 200°C. is reached.[263]

Considerable interest attaches to the $KCl-MgCl_2$ system and related systems because of the possibility of their application to the production of magnesium metal. The phase diagram, obtained by microscopical and *X*-ray examination, is reported as showing an unstable phase between 37·2% and 41·2% of magnesium chloride, which partially decomposes, exothermically, at 425°C. to form potassium chloride and $KCl,MgCl_2$.[264] The electrical conductivity isotherms over the range 600°–800°C. show a discontinuity between 27 and 37 mole% of magnesium chloride, whilst the temperature coefficients show a maximum at 33–34%. This suggests the existence of $2KCl,MgCl_2$ as a possible compound in the system.[265] Densities and electrical conductivities for the molten phase in the system up to 1000°C. are reported.[266,267] Transport number measurements have shown that as the composition changes to higher potassium chloride contents, up to a limit of $2KCl,MgCl_2$, the transport number of the magnesium falls.[268] Evidence for the compound $2KCl,MgCl_2$

is obtained from measurements of the internal friction in melts containing potassium and magnesium chlorides.[269] The solubility of magnesium metal in a mixture of magnesium and potassium chlorides at 800°–1300°C. is small compared with its solubility in pure molten magnesium chloride.[270]

TABLE VII.-BINARY SYSTEMS CONTAINING POTASSIUM CHLORIDE (CONTINUED)
(ALL COMPOSITIONS REFER TO MOLE% POTASSIUM CHLORIDE UNLESS OTHERWISE INDICATED)

System	Remarks	Reference
$KCl-MgSO_4$	Langbeinite, $K_2SO_4,2MgSO_4$, identified in solid phase	271
$KCl-CaCl_2$	Density measurements, 600°–900°C., over the whole range of composition	272
	Two eutectics at 608°C. and 17·5 mole%, and 590°C. and 60 mole%, respectively, and maximum in melting point curve corresponding to $2KCl,3CaCl_2$, m.p. 725°C.	205
	Temperature-composition diagram	273
	Change in density of KCl crystals on adding Ca ions up to ionic ratio of $2{\cdot}5 \times 10^{-4}$	274
	Concentration of thermodynamic vacancies obtained by measurement of conductivity of solid	275
$KCl-CaSO_4$	Temperature composition diagram	273
	Temperature composition diagram	276
$KCl-SrCl_2$	Distribution of $SrCl_2$ between solid and liquid KCl	277
	Change in density of KCl crystals on adding Sr ions up to ionic ratio $2{\cdot}5 \times 10^{-4}$	274
	Concentration of thermodynamic vacancies obtained by measurement of conductivity of solid	275
$KCl-BaF_2$	Eutectic at 739°C. and 86 mole%	229
	Eutectics at 575°, 616°, 625°, and 728°C.	278
$KCl-BaCl_2$	Compound $2KCl,BaCl_2$, m.p. 660°C.	229
	Eutectic at 645°C. and 57·25 mole%, transformation point at 656°C. corresponding to $3KCl,BaCl_2$	195
	Densities and molal volumes over the whole range of composition at 800°C.	279
	Surface tensions and their temperature coefficients	280
	Concentration of thermodynamic vacancies obtained by measurement of conductivity of solid	275
	Equilibria between fused alloy containing Ba metal and melt	281
$KCl-Ba(NO_3)_2$	Two double salts, KNO_3, KCl and $2KCl,BaCl_2$, found	282
KCl–Ba titanate	Solubility of Ba titanate <0·1%	283
$KCl-CeCl_3$	Temperature-composition diagrams	284
$KCl-K_2TiF_6$	Eutectic at 640°C. and 43 mole%	285
$KCl-ZrCl_4$	Phase diagram applied to preparation of high purity $ZrCl_4$	286
$KCl-MnCl_2$	Double salts observed	287
	Preparation of K_4MnCl_6 and KCl(Pb + Mn) phosphors	288
$KCl-CoSO_4$	3Eutectics and 5 transformation points	289
	2 compounds indicated, langbeinite and an unstable double sulphate of K and Co	276

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TABLE VII.-CONTINUED

System	Remarks	Reference
KCl–CuCl	Electrical conductivity studied	290
KCl–AgCl	Temperature coefficient of hardness determined	291
	Viscosity and electrical conductivity in melt	292
	Dielectric breakdown in mixed crystals (0·094 mole% AgCl)	293
	Anomalous dielectric dispersion in crystals containing 0·1% AgCl	220
KCl–AgBr	Eutectic at 318°C. and 23·5 mole%; reciprocal system KAg||ClBr studied	294
	Equilibrium constant for stable salt pair at 705°C. is 2·08	223
	Establishment of equilibrium	204 *b*
$KCl–AgNO_3$	Cryoscopic studies show deviation from ideal behaviour of KCl dissolved in $AgNO_3$	295
KCl–AgI	Phase diagram	296
	Equilibrium constants for stable salt pair at 698° and 752°C. are 2·89 and 2·08, respectively	223
$KCl–ZnCl_2$	Density measurements 350°–500°C. over the whole range of composition	272
$KCl–ZnSO_4$	Heat capacities of salt $KCl,ZnSO_4$ in range 500°–800°K.	297
	Densities in system 475°–550°C.	297 *a*
	Polarographic study of $2KCl,ZnSO_4$ at 375°C.	298
$KCl–CdCl_2$	Density of mixtures containing 80, 60, 40, and 20 mole% KCl	299
	Surface tension of mixture containing 68 mole% KCl over temperature range 600°–750°C., interfacial tension of molten Cd and $KCl–CdCl_2$ melt measured	300
	Electrical conductivity shows a maximum at 33 mole%, minimum at 50 mole%	301
	Viscosity and electrical conductivity isotherms	292
	Surface tension isotherms	249
$KCl–HgCl_2$	Phase diagram	301 *a*
$KCl–PbCl_2$	Viscosity isotherms and electrical conductivity	292
	Surface tension isotherms	249
	Transport number measured	302
	Anomalous dielectric dispersion in crystals containing 0·1% $PbCl_2$	220
	e.m.f. of cells using system as electrolyte	302 *a*
	Activity data and decomposition potential	302 *b*
$KCl–PbSO_4$	Agglomeration of equal amounts of powder	303
$KCl–AlCl_3$	Eutectic 133°C. and 34 mole%	304
	Relationship between density and composition irregular	305
	Decomposition potentials of various metal chlorides in $KCl–AlCl_3$ system as solvent	306
$KCl–AlBr_3$	Complexes, KCl,Al_2Br_6 m.p. 83·5°C., and $KCl,AlBr_3$ m.p. 171°C.	307
	Large increase in conductivity on dissolving KCl in $AlBr_3$	308

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TABLE VII.-CONTINUED

System	Remarks	Reference
KCl–cryolite	Cryoscopic data	309
KCl–TlCl	Anomalous dielectric dispersion in crystals containing 0·1% TlCl	220
KCl–Tl_2SO_4	System described	310
KCl–$SbCl_3$	Solubility of KCl determined, at 450°–470°C. and 2·4–5·9 by wt.-%KCl there are two liquid phases	311
	Electrical conductivity, a maximum found in plot of conductivity against viscosity	312
	Electrical conductivity at 98·5°C.	313
	Viscosity linear from 0·009 to 0·5N. at 100°C.	314
KCl–acetamide	Freezing point curve	315

TABLE VIII.-POLYCOMPONENT SYSTEMS CONTAINING POTASSIUM CHLORIDE (ALL COMPOSITIONS REFER TO MOLE% POTASSIUM CHLORIDE UNLESS OTHERWISE INDICATED)

System	Remarks	Reference
KCl–LiCl–NaCl	Eutectic at KCl 37 mole%, LiCl 51·5%, NaCl 11·5 mole%	194
KCl–LiCl–RbCl	Phase diagram	253
Reciprocal system K Li ‖ Cl SO_4 tungstate	Phase diagram	316
Reciprocal system K Na ‖ Cl Br I	Phase diagram	317
Reciprocal system K Na ‖ F Cl Br I	Phase diagram	318
KCl–KF–K_2CrO_4	Phase diagram	319
KCl–KNO_3–K_2SO_4	Eutectic at 318°C. containing 1, 16·7, and 82·25% K_2SO_4, KCl, and KNO_3, respectively	320
KCl–$KClO_3$–$KClO_4$	Phase diagram constructed, kinetic studies on the decomposition of $KClO_4$	321
KCl–NaCl–$MgCl_2$	Phase diagram	322
	Phase diagram (650° and 100°C.)	323
	Phase diagram, 3 ternary eutectics	324
KCl–NaCl–$MgCl_2$–$CaCl_2$	Phase diagram	325
	Densities and surface tensions	326
	Electrical conductance	327
	Decomposition potentials	327*a*
Reciprocal system K Na Mg ‖ Cl SO_4	Phase diagram	318
	Phase diagram	328
KCl–NaCl–$CaCl_2$	No ternary compounds formed	322
	Two ternary eutectics, (a) at 495°C., 5% KCl, 25% NaCl, 70% $CaCl_2$,, (b) at 530°C., 50% KCl, 20% NaCl, 30% $CaCl_2$	205
KCl–NaCl–$SrCl_2$	No compounds containing KCl formed	322
KCl–$MgCl_2$–$CaCl_2$	Phase diagram	329
KCl–$MgCl_2$–$BaCl_2$	Phase diagram	330
Reciprocal system K Na Ca ‖ Cl F	Phase diagram	331
KCl–NaCl–$CeCl_3$	Phase diagram	284
KCl–NaCl–K_2TiF_6	Eutectic at 710°C. containing 65% K_2TiF_6	285

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TABLE VIII.-CONTINUED

System	Remarks	Reference
$KCl-LiCl-TiCl_3$	Electrolyte for production of Ti metal	332
$KCl-CuCl-CuCl_2$	Phase diagram and equilibrium chlorine pressure measured	333
Reciprocal system K Na Zn || Cl SO_4	Phase diagram	334
$KCl-CdCl_2-PbCl_2$	Electrical conductivity measured and discussed in relation to viscosity and existence of compounds	310
$KCl-PbCl_2-PbS$	Metallic Pb obtained on electrolysis at 500°–550°C.	335
$KCl-NaCl-AlCl_3$	M.p. of ternary system measured, minimum m.p. lies below 100°C. at about 18–10 mole% KCl, 22–30 mole% NaCl, 58–62 mole% $AlCl_3$. Ternary eutectic at 93°C. and 14 mole% KCl, 26 mole% NaCl, 60 mole% $AlCl_3$	336
$KCl-AlCl_3-$ Nitrobenzene.	Electrochemical investigation	337
	Molar refractivity	338
$KCl-AlBr_3-$ Nitrobenzene.	Cryoscopic investigation	339
$KCl-AlBr_3-$ Ethyl bromide.	Electrochemical investigation	340
Reciprocal system Na K Tl || Cl NO_3 SO_4	Phase diagram	318

Aqueous Systems

The $KCl-H_2O$ system with a eutectic at −10·646 ± 0·0025°C. has been suggested as a fixed point in thermometry.[341] Solubility data to be found in Mellor, II, 540, have been considerably extended. Table IX summarises some of the additional data.

TABLE IX.-SOLUBILITY OF POTASSIUM CHLORIDE IN WATER

Temperature °C.	Solubility, g.KCl/100 g. H_2O	Reference
15	24·73	342
20	25·58	342
25	26·46	342
25	26·38	343
50	42·79	344
68	47·57	344
92	53·68	344
100	55·5	345
100	56·0	346
110	57·2	347
120	60·5	345
129	61·8	347
130	62·9	346
130	62·1	348
130	62·3	348
131	67·2	348
133	68·9	348

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TABLE IX.-CONTINUED

Temperature °C.	Solubility, g.KCl/100 g. H_2O	Reference
140	65·6	345
141	64·7	347
150	68·0	346
150	70·6	348
161	70·1	347
169·5	73·7	345
170	73·4	346
178	76·1	348
180	76·4	348
190	79·7	345
199	80·8	347
220	87·0	346
230	90·5	347
250	95·3	346
251	98·0	347
273	106·2	347
295	115·1	347
300	109·6	346
328	130·9	347
362	150·0	347
391	167·4	347
409	180·9	347
454	222·6	347

The solubility of potassium chloride in super-critical water at 400°–500°C. and 300 atmospheres has been measured; it increases with pressure, at constant temperature, according to the equation $L = kp^{3\cdot 2}$, where L is the solubility p is the pressure, and k a constant.[349] The solubility at high pressures, calculated at 25°C., is:

1000 atm.	27·4 g./100 g. water
2000	28·5
3000	29·6
4000	30·6
5000	31·2
6000	32·2
7000	33·2
8000	33·7
9000	35·7
10,000	37·1[350]

The solubility-temperature curve of potassium chloride shows inflections at 11°C., 22°C., and 27°C. It is suggested that these may correspond to crystalline modifications which have not been observed by X-ray methods.[351] The discontinuous change of the temperature coefficient of solubility at 21·2°C. has been discussed on thermodynamic grounds.[352]

The solubility of potassium chloride in deuterium oxide is rather less than that in water, the difference becoming less as the temperature rises. When the solubility is expressed in moles of solute per 55·51 moles of solvent, the difference at 30°C. is 7%, at 100°C. 3·6%, and at 180°C. 1·5%.[353] Table X shows the values at rounded temperatures expressed as moles of potassium chloride per 55·51 moles of solvent compared with those for water.[354]

The solubility of potassium chloride decreases in the presence of hydrochloric acid. At 25°C., in 10% hydrochloric acid, the solubility is 12% by

TABLE X.-SOLUBILITY OF POTASSIUM CHLORIDE IN WATER AND DEUTERIUM OXIDE

Temperature °C.	M water	M deuterium oxide
0	3·78	3·16
10	4·20	3·68
20	4·61	4·16
25	4·80	4·38
30	5·00	4·59
40	5·37	5·01
60	6·09	5·79
80	6·80	6·52
100	7·51	7·25
120	8·21	7·97
140	8·89	8·67
160	9·57	9·36
180	10·24	10·06

weight, in 20% hydrochloric acid, 4%.[355]

The critical temperature of aqueous potassium chloride solution of mole fraction 0·02618 is 700·3°K.;[356] of mole fraction 0·012245, 685·36°K.; of 0·006157, 671·26°K.; of 0·003081, 662·06°K.; of 0·00154·1, 655·71°K.; and of 0·000770, 651·91°K.[357] Equilibrium pressures of the potassium chloride-steam-saturated aqueous solution system have been measured between 250°C. and 600°C. A maximum pressure of 225 atm. was found at 565°C.[358]

The hydration number of potassium chloride, *i.e.* the total hydration of ions, in aqueous solution has been found to be 8·6 in a 1 M. solution; 10·2 in a 0·5 M. solution;[359] and 14 in a 2 M. solution.[360] An hydration number of 24 is obtained by calculation from data on the 'salting out' of oxygen and argon from aqueous solution by the addition of potassium chloride.[361] A further figure of 16·3 has been obtained from measurements of the distribution of butyric acid between benzene and aqueous potassium chloride.[362] Vapour pressure data have been applied to a study of the hydration of salts including potassium chloride.[363] The heat of hydration at 25°C. has been estimated as 159 kg.-cal./mole.[364]

The *X*-ray absorption spectrum of potassium chloride solutions has been observed over the concentration range 1·77 to 3·55 M.[365] The diffraction, or scattering effects, from potassium chloride solutions are not significantly different from those of water alone.[366]

In view of the importance of crystallisation from aqueous solutions in the isolation of potassium chloride, this aspect has received considerable attention. Problems concerning the caking of potassium chloride on storage have aroused interest in the crystal habit of the resulting crystals. The temperature of the first spontaneous crystallisation, T, and the saturation temperature, T_S, are connected by the expression $T_S - T = 13\sigma V_m/\lambda$, where σ is the specific surface energy, V_m the molecular volume, and λ the heat of solution.[367] The stability of supersaturated solutions[368] and the limits of supersaturation[369] are also related to solvent viscosity and solute concentration, although these effects are small for potassium chloride. Capillary-active substances, such as capryl alcohol, lower the limit of supersaturation; rather surprisingly, dyes raise this limit.[370] Experimental data on potassium chloride supersaturation have been used to confirm a theoretical relationship, $\lambda = k\lambda_0\,(T_1 - T_0)/[1 + k(T_1 - T_0)]$, where the supersaturation, λ, has a limiting value, λ_0, and T_1 is the supersaturation temperature, and T_0 the temperature at which the solution would be saturated, k is a constant.[371] The value of the supersaturation of potassium chloride solution at 20°C., ρ, is 0·095, and is given by the expression $\rho = c - c_0/c_0$, where c_0 is the solubility at which no spontaneous crystallisation is observed. For the temperature range 0°–40°C., $\rho = 13{\cdot}48(\mathrm{d}\ln c_0/\mathrm{d}T)$.[372] The formation and growth of crystal nuclei in the crystallisation process have received some attention,[373,374] and there is evidence to support their existence.[375] The number of nuclei formed at 64°C., on cooling a solution saturated with potassium chloride, is greater when sodium chloride is also present than with potassium chloride alone.[376] From cooling curves, it appears that the rate of crystallisation depends on the square of the supersaturation as expressed in degrees, and is a linear function of the number of nuclei and of the total surface area of the seeds. The rate also depends on the surface form of the nuclei.[377] The difference between the saturation and crystallisation temperatures when solutions are slowly cooled with continuous agitation has been measured, and the normal solubility at various temperatures has been compared with the corresponding value of the supersolubility limit.[378] The temperatures at which potassium chloride deposits from solutions saturated at 40°C.[379] and 50°C.,[380] have been found to be a function of the rate of cooling. As part of a general thermodynamic study of the factors affecting the rate of nucleation from supersaturated solutions,[381] the role of free electric charges[380,381] at the surfaces of nuclei has been discussed, with particular reference to potassium chloride. The surface energy of formation of crystal nuclei in such solutions has been calculated on the basis that spontaneous nucleation occurs at a particle size of 10^{-7} cm.[382] The degree of supersaturation and the rate of evaporation alone determine the crystal habit. Impurites, such as the chlorides of magnesium, manganese, lead and cadmium, and sodium carbonate and urea, act only in lowering the degree of supersaturation at which, in their absence, habit changes would otherwise occur. Such changes, including dendritic growth, are attributed to solvation of the surface ions of the crystal by the solvent.[383–385] A bibliography of 31 papers in this field has been published.[383]

The effect of numerous dyes on the mode of growth of potassium chloride crystals has been investigated,[386,387] and 107 references have been listed.[387] Slow evaporation of solutions of the salt on glass[385,388] or platinum surfaces under controlled conditions of temperature and desiccation results in the development of [100] faces only, while above a certain critical rate of evaporation octahedral crystals appear.[385] A solution of potassium chloride rapidly evaporated at low pressure gives a mixture of cubic, linear, dendritic, and irregular dendritic crystals, the last two being unstable under the electron microscope.[389] Translucent specimens have been obtained both from pure aqueous solutions and from those containing various impurities. From acidified solutions containing Th^{4+} (8×10^{-3} g.ion/l.), large transparent cubes can be grown; and from solutions containing Bi^{3+}, transparent pyramidal crystals. With a potassium chloride solution containing lead ions at concentrations exceeding 8×10^{-4} g.ion/l., large cubo-octahedra are formed, of which the [100] faces are transparent and the [110] faces are translucent, the lack of transparency being due to the presence in the crystal of a pattern of numerous minute cavities filled with mother liquor.[390–392] A higher concentration of lead or tin impurity (0·1 g.ion/l.) promotes the development of a transparent octahedral form which retains traces of ion impurities and fluoresces under ultra-violet radiation. Both bismuth and antimony ions induce the growth of semi-transparent cubic crystals of potassium chloride from aqueous solution.[393] The octahedral and cubo-octahedral varieties are also obtained in the presence of lead chloride, bromide, and iodide, and of mercuric chloride.[394] Stelliform crystals may be grown from solutions containing bismuth ion.[395] The dendritic variety is formed both in pure aqueous solutions and in those containing various impurities.[396] The seeding of supersaturated solutions of the salt with insoluble binary compounds, of which the unit cell dimensions approximate to those of potassium chloride, such as the sulphide, selenide, and telluride of lead, and tin telluride, has been investigated by an electrical conductivity method. No simple relation obtains, however, between the ability of such substances to promote nucleation and the dimensions of their lattice constants in relation to those of the solute. It appears that other factors such as the chemical nature, the surface structure, and the particle size distribution of the seeds all contribute to the property in question.[397] The growth of sheet and fibrous varieties of the salt from hot-filtered saturated solutions which are subsequently cooled slowly, is to some extent inhibited by agar, gelatin, and lead chloride. The fibrous form is also deposited slowly from solutions containing ethylene glycol, and all the additives mentioned exhibit the Tyndall effect during crystallisation.[398] The formation of fibrous potassium chloride has been confirmed.[399] Contrary statements have, however, been made to the effect that the tendency of the salt to form dendrites on slow evaporation of its solution is increased by the presence of gelatin, agar, and glycerol. Furthermore, it is stated that suppression of dendritic growth occurs with gelatin when the chlorides of nickel and cobalt, or ferric chloride, are present separately in concentrations of 0·178, 0·194, and 0·041 mole/l., respectively.[400-402] By slowly evaporating solutions of potassium chloride in methyl alcohol, ethyl alcohol, acetone, acetophenone or dioxan, cubic crystals are obtained. More rapid evaporation yields octahedra, except for solutions in dioxan, when the [111] face is absent. The rate of formation of the [111] face has been studied in terms of the dielectric constant of the various solvents and of solvation effects.[403] Overgrowths of potassium chloride from the vapour phase and from solution onto the cleavage surfaces of mica,[404-406] calcium carbonate, and sodium nitrate[407] have been described and their mode of formation discussed. The deposition of films of the salt by vacuum evaporation onto cleavage surfaces of crystals of the chloride of lithium, sodium, and potassium, and of potassium bromide has also been investigated.[408] The oriented overgrowth of platinum films on the cube face of potassium chloride has been studied.[409] Thin vacuum-deposited films of sodium chloride on potassium chloride are oriented partly in accordance with the mode of growth of the base crystal and partly in the twin position [111] to the latter.[410] Overgrowths from the vapour phase onto silver crystals[411] and feldspar[412,413] have been investigated. On the heat-activated base, monocrystal films parallel to [111] are obtained.[413] Unlike the iodides of ammonium, potassium and rubidium, which do not orient mutually with potassium chloride, the chlorides and bromides of lithium, silver and rubidium, the cyanides of sodium and potassium, and also potassium fluoride, all form regular overgrowths on potassium chloride.[414] The general mechanism of overgrowth onto a potassium chloride base of lithium bromide, silver chloride, sodium chloride, and rubidium iodide, has been considered theoretically and examined experimentally.[415] The climbing growth of needle-like crystals of the salt from aqueous solutions has been ascribed to the action of capillary hollows,[416,417] and to ionic effects.[417,418] The conditions affecting grain size during the industrial production of potassium chloride[419] and the precipitation of potassium chloride from sea-water by progressive freezing, have been investigated.[420] In this process crystallisation of the salt, together with magnesium chloride dodecahydrate, occurs at −36°C., no carnallite being formed. A method of growing large homogeneous single crystals of potassium chloride by carefully controlled cooling from the molten state[421] has been described, with reference to the preparation of crystals suitable for optical, photochemical and electrical measurements. A modification of the original technique yields potassium chloride crystals up to 15 cm. across,[422] but under certain conditions of cooling the salt crystallises dendritically.[423] Twinning of the potassium chloride crystal occurs in the presence of the chlorides of sodium, strontium, and lead, and of potassium chlorate.[424] The removal of adhering anions from potassium chloride crystals follows the Hofmeister series in acidic and alkaline media.[425]

Etching, and the rates of dissolution of selected crystal faces of potassium chloride,[427] have been investigated in detail under controlled conditions of solvent flow, and of agitation. The first cavities arise along those lines of the crystal that are characterised by the densest packing of the atoms.[426] An expression relating K, the constant of the speed of dissolution; D, the coefficient of diffusion of the solute; v, the kinematic viscosity of the solution; l, the length (in cm.) of the side of the free surface of the crystal exposed to solvent action; and V, the speed of the crystal with regard to the solution in cm./sec., is given as $Kl/v = A(Vl/v)^{\alpha}(v/D)^{\beta}$. A and β are temperature-dependent terms, and α is a constant based on the solubility of the crystal under compensating conditions, for KCl $\alpha = 0{\cdot}5$, $\beta = 0{\cdot}37$.[427] The rate of solution of potassium chloride in water has been expressed, simply, by the equation: $\mathrm{d}n/\mathrm{d}t = KS(C - c)$, where $\mathrm{d}n$ is the amount dissolving in time $\mathrm{d}t$; S is the free surface area of the crystal; C is the solubility; c is the concentration in g./c.c. in the solvent at any given time; and K is a velocity constant.[428] The rate of solution has also been given as equal to the expression: $0{\cdot}790(G_1^{1/3} - G_2^{1/3})/Z$, where $(G_1^{1/3} - G_2^{1/3})$ is the loss in weight of a dissolving crystal during a time interval, Z. This expression was derived from measurements of the rate of solution of potassium chloride crystals in water, and in potassium and sodium chloride solutions, at various temperatures in the range 23°–90°C.[429] Rates of dissolution of mineral potassium chloride in water, in aqueous solutions of calcium and magnesium chlorides, and in an aqueous mixture of sodium, potassium, and magnesium chlorides, have been investigated extensively. The results, which are applicable to the study of the extraction of potassium chloride from various saline minerals, have been discussed on the basis of the kinetics of solution processes, and shown to be of a diffusion type between 0°C. and 100°C.[430]

Pycnometric precision methods have been used to determine the densities of dilute aqueous potassium chloride, and values accurate to 1 p.p.m. are now available. The densities at 0°C. of 0·099271, 0·1, and 0·01 M. solutions are 1·004840, 1·004881, and 1·00372 g./c.c., respectively;[431] for a 1·0 M. solution it is $1{\cdot}0480_4$ g./c.c.[432] The data at 18°C. are shown in Table XI.[433]

TABLE XI.- THE DENSITIES OF POTASSIUM CHLORIDE SOLUTIONS AT 18°C.

g./1000 g. water	Density g./c.c.
16·445	1·008996
4·132	1·001316
2·873	1·000502
0·9349	0·999237
0·6323	0·999038
0·4087	0·998890
0·2833	0·998808
0·1836	0·998744

There is a contraction of 12·3 c.c. on the dissolution of 1 g. mole of potassium chloride at infinite dilution at 18°C.[433] The densities of 0·1, 0·2, 0·5, 1·0, 3·0, and 4·0 M. potassium chloride solutions at 25°C. ± 0·02°C. are 1·0018, 1·0064, 1·0199, 1·0416, 1·1188, and 1·1528 g./c.c.[434] For 0·008607, 0·013096, 0·015290, 0·156666, 0·34601 and 0·59997 M. solutions at 25°C. the densities are 0·997486, 0·997695, 0·997802, 1·004460, 1·012999 and 1·024303 g./ml.[435] The apparent molal volume at 25°C. of potassium chloride solution is given by the expression: $\phi_{KCl} = 26{\cdot}50 + 3{\cdot}26\sqrt{m} - 1{\cdot}12m$, where m is the molality.[435] The density of potassium chloride solution can be expressed by the equation: $\rho^{25}_{4} = 0{\cdot}997074 + 0{\cdot}047896c - 0{\cdot}002069c^{1{\cdot}5}$,[436] where c = no. of moles per litre of solution. At 35°C., the apparent molal volume, ϕ, is given by the expression: $27{\cdot}303 + 2{\cdot}1c^{1/2} - 5{\cdot}6 \times 10^{-2}c$; and the specific gravity, S, is given by the expression: $1 + 4{\cdot}7696 \times 10^{-2}c + 2{\cdot}1 \times 10^{-3}c^{1{\cdot}5} + 5{\cdot}6 \times 10^{-5}c^{2}$. The equation for the specific gravity holds to within 5 p.p.m. between 0·0002 and 0·4 M.[437] The apparent molal volumes of 2·6914 molar (at 25°C.) aqueous potassium chloride at 85°, 65°, 45°, and 25°C., are 31·00, 31·17, 30·95, and 30·32, respectively.[438] The coefficients of apparent molal thermal expansion of potassium chloride solution are[439]

0·0618 c.c./mole/°C.	at 25°C. and 0·99817 molal,
0·0404	at 35°C. and 0·99476 *m.*
0·0238	at 45°C. and 0·99074 *m.*
0·0101	at 55°C. and 0·98620 *m.*
–0·0020	at 65°C. and 0·98118 *m.*
–0·0128	at 76°C. and 0·97571 *m.*

The integral heat of solution in g.- calories per mole of crystalline potassium chloride is reported as –3692 on formation of a saturated solution at 25°C.,[440] –4373 ± 2 at 20°C., and –4191 ± 2 at 25°C. on dilution to KCl, 200 H_2O.[441] –4600 on solution to form the eutectic mixture at –10·7°C.;[442] –4332 at 21·0°C. on dilution to KCl, 150 H_2O;[443] and on dilution to KCl, 200 H_2O, –4668 ± 6 at 12·5°C.,[444] –4196 at 25°C.;[445] and at 20°C. –4376 ± 0·1%,[446],[447] and 4244 ± 5.[448] The integral heat of solution of potassium chloride at 50°C. decreases linearly with increasing molal concentration. For a 0·138 molal solution, the value of $\Delta H_{\text{solution}}$ in g.-cal./mole is +3420; for a 0·521 *m.* solution, 3380; for 1·110 *m.*, 3351; 2·216 *m.*, 3256; for 2·828 *m.*, 3249; and for 4·744 *m.*, 3212, respectively. Values for $d(\Delta H)/dT$, for the temperature range 12·5°–25°C., decrease from 42·4 for 0·0 molal to 37·2 for 0·33 molal potassium chloride. For the range 25°–50°C., values of potassium chloride molality and temperature coefficient, $d(\Delta H)/dT$, respectively, are:

m	0·055,	0·16,	0·33,	1·11,	2·77,	4·44,	4·82.
$d(\Delta H)/dT$	30·0,	31·2,	31·6,	30·8,	25·8,	20·8,	19·6.

For the range 25°–75°C. the temperature coefficient is 31·7 in 0·16 molal potassium chloride.[449]

Small differences in the heat of solution between samples with different thermal histories have been reported. Thus, the difference in a sample fused and rapidly cooled and one that has been annealed, is of the order of 0·1 g.-cal./g. Similar small differences have been reported for crystals containing 0·2 mole% of copper (II) chloride or lead (II) chloride.[450] However, this small difference may not be significant compared with the experimental error.[451] The heat of solution in deuterium oxide with a D/(D+H) ratio of 0·98 is –4·809 g.-cal./mole at 25°C., on solution of 0·366 mole of potassium chloride in 100 moles of deuterium oxide. The difference between the heat of solution in deuterium oxide and in water is 560 kg.-cal.[452] The integral heat of solution of potassium chloride in hydrochloric acid on dilution to KCl, 1000 H_2O increases with increasing acid concentration.[453]

Heats of dilution have been measured with precision.[454],[455] The heats of dilution of potassium chloride are proportional to ionic strengths in very dilute solutions. The heat of dilution at various temperatures, t°, for concentrations c_v to c_n expressed in mole/litre, have been calculated from the equation: $u = 611(1 - 0{\cdot}017t)(c_v - c_n) + (209 + 4{\cdot}5t)(\sqrt{c_v} - \sqrt{c_n})$.[456] The heat of dilution at 0°C. from KCl, 25 H_2O to KCl, 50 H_2O is –752; to KCl, 100 H_2O, –1150; to KCl, 200 H_2O, –1371; and to KCl, 400 H_2O, –1446 Joules.[457]

The apparent molal heat capacity of potassium chloride solution is given by the expression: $\phi_c = -29{\cdot}0 + 11{\cdot}2\sqrt{m}$., where m is the molality.[458] The specific heat over the range 15°–45°C. of aqueous solutions of molarity: 0·1, 0·5, 0·75, 1·5, 2·0, and 2·50 is 0·9885, 0·9560, 0·9318, 0·8722, 0·8390, and 0·8138 g.-cal./°C./g. of solution.[459] The specific heats (g.-cal./°C./g. of solution) of potassium chloride of concentrations of 2·000, 1·000, 0·500, and 0·100 molality, respectively, are:

at 10°C., 0·8423, 0·9144, 0·9512, and 0·9868;
at 20°C., 0·8439, 0·9131, 0·9526, and 0·9862;
at 30°C., 0·8457, 0·9148, 0·9539, and 0·9856;
at 40°C., 0·8474, 0·9166, 0·9555, and 0·9850.

The data at 15°, 25°, and 35°C. are also given.[460] Data for 16·9–24·8% potassium chloride over the temperature range 16°–34°C. are reported.[461] At 20°C., the specific heat of a solution corresponding to $KCl,25H_2O$ is given as 0·83078; at 50°C., 0·8377; and at 80°C., 0·8390.[462]

Information on the freezing point depression of potassium chloride solutions (Mellor, II, 547), has been extended by more precise data, often quoted alongside other thermodynamic measurements.[463] The Lewis and Randall function, $j = (1-\theta)/3{\cdot}716m$., where θ is the depression of freezing point, and m is the molality, is related to the concentration by the expression: $j = (0{\cdot}3738\sqrt{m}/1 + 1{\cdot}7\sqrt{m}) + 0{\cdot}0149\,m$. Experimental results fit this equation well.[464] Solutions of potassium chloride have depressions as follows: 0·001 m 0·00365° C.; 0·005 m., 0·01820°C.; and 0·01 m., 0·0360°C.; the figures being in good agreement with data calculated by the Debye and Hückel equation.[465]

Numerous precision measurements of the vapour pressure are reported, with results in close accord with Raoult's Law.[466] The osmotic coefficient at 25°C., ϕ, has been evaluated as $(-55{\cdot}5062/2\,M)\ln P/P_0$, where M is the molarity, P_0 is the vapour pressure of water, and P the vapour pressure of the solution. Experimental data fit this equation.[467] Table XII gives the vapour pressure in mm. of mercury at 25°C., obtained by the following methods: dew point,[468] dynamic,[469] static,[470] and e.m.f. (through activity measurements derived from the concentration cell $Ag/AgCl(s)/KCl,\ c_1/K_xHg/KCl, c_2/AgCl(s)/Ag$).[471]

TABLE XII.-VAPOUR PRESSURE OF POTASSIUM CHLORIDE SOLUTIONS AT 25°C. BY VARIOUS METHODS

M.	Dew Point	Dynamic	Static	e.m.f.
0·25	23·56	23·56	23·57	–
0·375	23·46	23·47	23·47	23·49
0·750	23·20	23·19	23·20	23·21
1·000	23·03	23·02	23·01	23·02

Abnormally high vapour pressures of solutions containing about 58 g. of potassium chloride per 1000 g. of water have been reported,[472] but these have not been substantiated and it is probable that they are due to the solution being 'metastable'.[471] The vapour pressure of a saturated solution over the temperature range 0°–25°C. is given by the expression:

$$\log P = (-2995{\cdot}5/T) - 6{\cdot}680\log T + 0{\cdot}001024T + 27{\cdot}569.$$

The values calculated from this equation lie within ± 0·05 mm. of the experimentally observed pressures.[473] Vapour pressure data for saturated potassium chloride solutions over the temperature range 19–30°C.[474] and 33·6–44·0°C.[475] are presented in Table XIII, and over the range 55–105°C. in Table XIV.[476] From measurements of the boiling point of a solution of potassium chloride containing 20 g./100 g. of water, the vapour pressure at 178·9°C. is found to be 6995 mm.;

TABLE XIII.-VAPOUR PRESSURE OF SATURATED POTASSIUM CHLORIDE SOLUTIONS OVER THE RANGES 19°–30°C. AND 33·6°–44·0°C.

t°C.	P m.m.
19	13·97
20	14·97
21	15·98
22	17·01
23	18·05
24	19·10
25	20·20
26	21·37
27	22·64
28	23·99
29	25·37
30	26·88
33·6	32·46
39·3	43·70
44·03	55·62

TABLE XIV.-VAPOUR PRESSURE OF SATURATED POTASSIUM CHLORIDE SOLUTIONS OVER THE RANGE 55°–105°C.

t°C.	P mm.
55·0	98·0
60·0	123·0
65·0	152·0
70·0	187·0
75·0	232·0
80·0	283·0
85·0	342·0
90·0	406·0
95·0	490·0
100·0	584·0
105·0	688·0

at 188·9°C., 8642 mm.; at 198·9°C., 10,643 mm.; and at 208·3°C., 12,964 mm.[477] The vapour pressure of supersaturated solutions has been measured over the temperature range 30°–40°C. for a solution containing 32·5 g. per 100 g. of water, by the dew point method; no data are given, but the pressure is said to follow the equation: $\ln p = -10{,}000/RT + 8{\cdot}5701$. No abrupt change in the vapour pressure-temperature curve occurs as the supersaturated region is approached.[478] The volatility of potassium chloride on evaporation, referred to in Mellor, II, 535, has been confirmed by one worker, who finds that there is an increased carrying over of salt with increase of concentration of the solution,[479] and denied by another, who finds no volatility from a 0·1 M. solution.[480]

The compressibility of potassium chloride solutions between 30° and 80°C., for a pressure range of 1–200 atm. is a linear function of the concentration, as the following data show:

% KCl		2·59,	5·37,	10·40,	12·23,	17·92,	22·19
Compressibility 0–100 atm. × 10^6	at 30°C.	42·9,	41·2,	38·5,	37·5,	34·7,	32·8
	at 80°C.	44·0,	42·2,	39·7,	38·6,	35·8,	33·9

An increase of pressure from 1 to 1000 bars at 25°C. on aqueous potassium chloride containing, respectively, 5·88, 10·91, 13·79, 16·84, 20·00, 23·22, and 25·52 g. per 100 g. water produces a decrease in volume per unit volume of 0·03632, 0·03422, 0·03302, 0·03167, 0·03039, 0·02929, and 0·02846.[482] For a 1% potassium chloride solution, the mean compressibility at 29·97°C. can be represented by the expression, (p is in atmospheres): $44{\cdot}25 \times 10^{-6} - 5{\cdot}37 \times 10^{-9}p$; for a 2·687% solution, $43{\cdot}00 \times 10^{-6} - 5{\cdot}00 \times 10^{-9}p$; for a 5·233% solution, $41{\cdot}83 \times 10^{-6} - 4{\cdot}91 \times 10^{-9}p$.[483]

The relative viscosity (η), at 25°C., of solutions at various molar concentrations is expressed by the equation: $\eta = 1 + 0{\cdot}0052\sqrt{c} - 0{\cdot}01612c + 0{\cdot}00808c^2$. The minimum viscosity is at a concentration of 0·8 M. The equation holds up to a concentration of 3 M.[484,485] The viscosity at 18°C. is given by the expression: $\eta_c = \eta_0(1 + 0{\cdot}0046\sqrt{c})$, where c is the molar concentration, and η_0 is the viscosity of water.[486,487] The temperature variation of viscosity is shown by the values in Table XV.[487]

TABLE XV.-TEMPERATURE VARIATION OF VISCOSITY, η, OF POTASSIUM CHLORIDE SOLUTIONS

Concn. M.	18°C.	30°C.	40°C.	50°C.	60°C.	70°C.	80°C.	85°C.
0·0500	0·9997	1·0008	1·0018	1·0027	1·0034	1·0043	1·0047	1·0046
0·1000	0·9984	1·0014	1·0034	1·0041	1·0056	1·0069	1·0082	1·0083
0·5000	0·9896	1·0041	1·0131	1·0196	1·0256	1·0321	1·0368	1·0382
1·000	0·9837	1·0098	1·0273	1·0406	1·0528	1·0627	1·0717	1·0747

The variation of viscosity with absolute temperature has been shown to follow Andrade's relationship closely.[488]

The osmotic pressure at 26·429°C. has been measured directly as 96·5, 136·5 and 187 mm. of mercury in 0·0020, 0·00298, and 0·00504 molal solutions of potassium chloride.[489]

The refractive indices of aqueous solutions of potassium chloride (Mellor, II, 549–550, and Table XX) have been extended by more precise measurements and by the addition of data at further concentrations and temperatures. The variation of refractive index with temperature and concentration is shown graphically in Fig. I.[490] Data over the concentration range 0·001 to 4 M. at 25°C. show that the molar refraction, R_{25}, has a maximum of 11·299 between 0·2 and 0·5 M. and falls to 11·268 at 0·01 M., and to 11·235 as the concentration tends to zero.[491] The molar refraction with helium D_3 line at 25°C. is given in Table XVI.[492]

TABLE XVI.-MOLAR REFRACTIVITY OF POTASSIUM CHLORIDE SOLUTIONS AT 25°C.

Molar concentration	Molar refractivity
0·02	11·228
0·04	11·240
0·06	11·252
0·08	11·258
0·10	11·264
0·12	11·264

The variation with concentration (c, in moles per litre) of the difference in refractive index, Δn, between water and the aqueous solution of potassium chloride is given by the expression: $(\Delta n/c)_{25} = 0{\cdot}010230 - 0{\cdot}00137c$.[492] The refractive indices[493] at 20°C. and 25°C. are shown in Table XVII. Values of −7·5°C. and −9·8°C., and of −3·5°C. and −3·6°C., have been obtained for the temperatures of maximum refractive index of 0·5 and 0·25 M. solutions of potassium chloride, respectively.[494]

Variation of refractive index of more concentrated solutions with concentration is indicated by the following data:

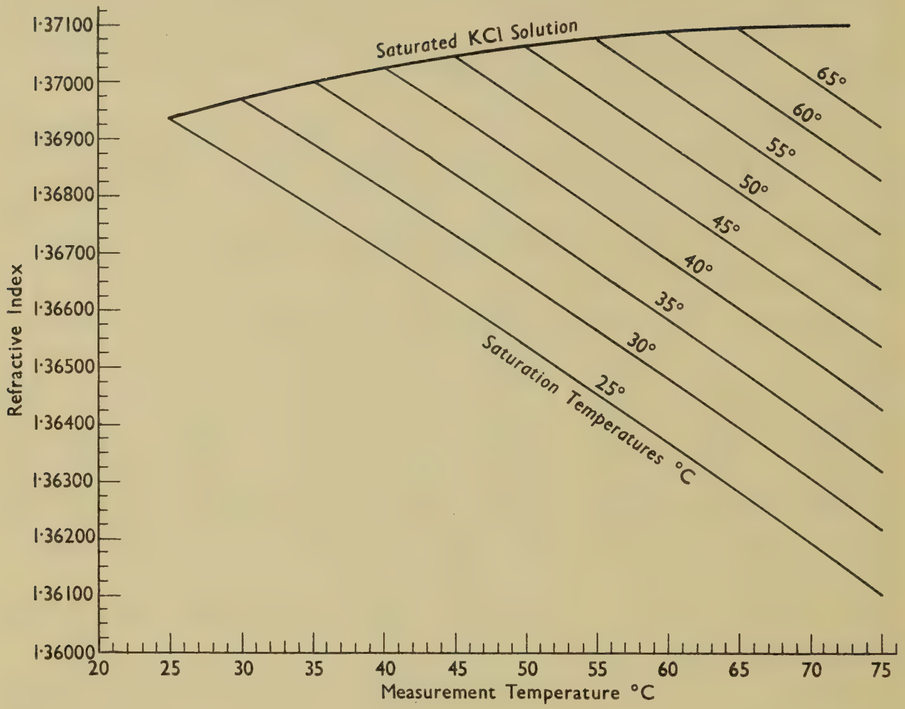

FIG 1.-VARIATION OF REFRACTIVE INDEX WITH TEMPERATURE AND CONCENTRATION OF POTASSIUM CHLORIDE SOLUTIONS

TABLE XVII.-REFRACTIVE INDICES OF POTASSIUM CHLORIDE SOLUTIONS AT 20°C. AND 25°C.

	0·099805 Molal		
t°C.	*n*(λ = 6563 A.)	*n*(λ = 5890 A.)	*n*(λ = 4862 A.)
20	1·332271$_9$	1·334131$_5$	1·338246$_7$
25		1·333602$_5$	
	0·019938 Molal		
20	1·331419$_5$	1·333279$_2$	1·337392$_2$
25	1·330946$_5$	1·332756$_9$	1·336928$_7$

Concentration, Molal	$n^{25}_{D_3}$	$R^{25}_{D_3}$
1·1323	1·34294$_0$	11·296
1·4927	1·34612$_1$	11·303
2·2073	1·35173$_5$	11·300
3·0312	1·35769$_5$	11·292
4·4104	1·36670$_5$	11·289
4·4246	1·36678$_5$	11·284[495]

The figures below show the variation of refractive index with temperature: The molecular absorption coefficient of aqueous solutions of potassium chloride has been determined in the region λ = 4000–25000 A.[497] The light

t°C.	Concentration Molal	n_{D_3}	R_{D_3}
25			
25	1·2983	1·34460	11·313
35	1·2982	1·34325	11·355
45	1·2980	1·34168	11·382[496]

scattering, or Rayleigh effect, measured for potassium chloride solutions of concentrations above 0·1M., is less than the theoretical,[498] the deviations increasing as the concentration increases.[499]

The Faraday effect, the magneto-optic rotation, (Partington, "Advanced Treatise on Physical Chemistry", IV,592,602) for potassium chloride has been investigated, and the Verdet constant reported.[500] The molar rotativity and the molar refractivity, both extrapolated to infinite dilution, are 3·80 × 10^{-10} min.sq.cm., and 11·313, respectively.[501] Variation of the molar rotativity with concentration, at 0°C., has been reported.[502]

The surface tension of potassium chloride solution is said to be less than that of water at certain concentrations, and to pass through a minimum at about 0·001M., the measurements being made by the capillary height[503] and ring[504] methods. A theoretical treatment has led to a formula for the surface tension of potassium chloride solutions in accord with these results.[505] However, the existence of this minimum has not been confirmed in a determination using a precision ring method,[506] nor by use of the differential bubble pressure method. Further, the results of this latter method are in complete accord with the Onsager-Samaras equation.[507] The explanation probably lies in the fact that the capillary height and ring methods have ignored the zeta-potential at the silica solution interface. The relative surface tensions (γ/γ_{H_2O}) by the bubble pressure method at 25°C. ± 0·01°C. are: 1·000097 at 0·00229M., 1·000138 at 0·00481M., 1·00142 at 0·0437M. and 1·00179 at 0·0512M.[507] The surface tension of an aqueous solution of potassium chloride at 25°C. is given by the expression: $\gamma = km + \gamma_0$, where m is the molality, γ_0 is the surface tension of water, and k is a constant. Surface tension data and values of k are given in Table XVII.

TABLE XVII.-SURFACE TENSIONS OF POTASSIUM CHLORIDE SOLUTIONS AT 25°C. (DYNES/CM.)

	Molality	γ	k
Maximum bubble pressure method[508]	1·000	73·68	1·67
	2·010	75·34	1·65
	3·051	76·73	1·55
	4·015	78·14	1·53
Drop weight method[509]	1·00	74·55	
	2·00	76·13	
	3·00	77·77	
	3·80	79·17	
Stalagmometry[510]	1·0	73·64	
	2·0	75·06	
	4·0	77·85	
	4·83 (saturated solution)	78·95	

Table XVIII shows data at 20°C. and 40°C.[511] Surface tension data are also available for various concentrations at 0°C.,[512] and 5°–35°C., in 5° intervals.[513] The effect of adding hydrochloric acid to potassium chloride solution is to reduce the surface tension by a small amount, as shown in Table XIX,[514] where the observed values are compared with the values calculated (γ calc.)

TABLE XVIII.-SURFACE TENSIONS OF POTASSIUM CHLORIDE SOLUTIONS AT 20°C. AND 40°C. (DYNES/CM.)

% KCl	γ at 20°C.	γ at 40°C.
4·72	73·60	70·61
9·85	74·83	71·82
14·41	75·99	72·97

for a simple mixture of two electrolytes.

TABLE XIX.-SURFACE TENSIONS OF POTASSIUM CHLORIDE SOLUTIONS CONTAINING HYDROCHLORIC ACID, AT 25°C.

Concentration molal KCl	Concentration molal HCl	γ exp.	γ calc.
1·015	0·1	73·60	73·69
2·018	0·1	74·98	75·52
3·032	0·1	76·52	76·61
4·033	0·1	77·69	78·15

Interfacial tensions between potassium chloride solutions and *n*-hexane have been measured over a range of concentrations by both static and dynamic methods.[515] The interfacial tension between mercury and a molar solution of potassium chloride at 20°C. is 357·5 ergs/sq.cm.[516]

The electrical conductivity of aqueous potassium chloride solutions has attracted considerable attention, both as a test of current electrolyte theory, and as a readily accessible standard for the calibration of conductance cells. In consequence there is a substantial literature, covering many determinations over a wide range of concentrations and temperatures, the salient points of which are given below.

The precautions needed in obtaining precision data such as the use of correctly defined units of concentration, the purity of the water and the potassium chloride employed, and the design and layout of the cell and associated measuring apparatus, have received much attention.[517-524] A considerable effort has been made to obtain data of suitable precision for cell constant measurements. Table XX, taken from H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", American Chemical Society Monograph Series, Third Edition, New York, 1958, sets out the data in such a way as to facilitate conversion of the various concentration terms. By far the most satisfactory standards for the measurement of cell constants are those of Jones and Bradshaw. All the data on conductivity in aqueous solution which follow are based on grams of potassium chloride per 1000 grams of solution (all weights corrected to vacuum), expressed also in terms of normality or the demal ($1D$ = 1 g.-mol. dissolved in 1 cubic decimetre of solution at 0°C.)

Values of the equivalent conductivity at 25°C. can be calculated from the Onsager equation: $\Lambda = 149{\cdot}98 - 94{\cdot}5\sqrt{c}$, covering a range of concentration from $1{\cdot}1556$ to $10{\cdot}092 \times 10^{-4}$ M.[527] In other equations for data at 25°C., further terms have been found necessary, and equations such as those following have been proposed to represent the data: $\Lambda = 149{\cdot}92 - 93{\cdot}85\sqrt{c} + 50c$ (up to a concentration of 0·003 M.);[519,520] $149{\cdot}86 = (\Lambda + 59{\cdot}79\sqrt{c})/(1 - 0{\cdot}2274\sqrt{c}) - 94{\cdot}9c$ (for a concentration range 0·00003–0·1 M.),[528] and $149{\cdot}88 = (\Lambda + 60{\cdot}19\sqrt{c})/(1 - 0{\cdot}2289\sqrt{c}) - 145{\cdot}0c + 30c \log c$ (for concentration range $0{\cdot}5506$ to $17{\cdot}7312 \times 10^{-3}$ M.[521] Data at other temperatures (within the range 5°–55°C.) are represented by the equation: $\Lambda_0 = \Lambda + (B_1\Lambda + B_2)\sqrt{c}/1 + (3{\cdot}3B - B_1)\sqrt{c}$, where Λ_0, B_1, B_2, and B at various temperatures have the values shown in Table XXI.[529]

TABLE XX.-SPECIFIC CONDUCTIVITY OF STANDARD POTASSIUM CHLORIDE SOLUTIONS IN OHM^{-1}CM.$^{-1}$

	0°C.	18°C.	20°C.	25°C.
1 N-KCl (71·3828 g. KCl per kg. of solution in vacuum)				
Kohlrausch *et al.*[525]	0·06541	0·09822	0·10207	0·11180
Parker *et al.*[526]	$0{\cdot}06531_2$	$0{\cdot}09811_6$		$0{\cdot}11168_7$
Jones *et al.*[522]	$0{\cdot}06543_0$	$0{\cdot}09820_1$	$0{\cdot}10202_4$	$0{\cdot}11173_3$
0·1 N-KCl (7·43344 g. KCl)				
Kohlrausch	0·00715	0·01119	0·01167	0·01288
Parker	$0{\cdot}007141_6$	$0{\cdot}011184_6$		$0{\cdot}012876_5$
Jones	$0{\cdot}007154_3$	$0{\cdot}011191_9$	$0{\cdot}011667_6$	$0{\cdot}012886_2$
0·01 N-KCl (0·746558 g. KCl)				
Kohlrausch	0·000776	0·001225	0·001278	0·001413
Parker	$0{\cdot}0007742_2$	$0{\cdot}0012223_8$		$0{\cdot}0014103_7$
Jones	$0{\cdot}0007751_2$	$0{\cdot}0012226_9$	$0{\cdot}0012757_2$	$0{\cdot}0014114_5$
1 *D*KCl (71·1352 g. KCl)				
Parker	$0{\cdot}06509_8$	$0{\cdot}09779_0$		$0{\cdot}11132_2$
Jones	$0{\cdot}06517_6$	$0{\cdot}09783_8$		$0{\cdot}11134_2$
0·01 *D*KCl (7·41913 g. KCl)				
Parker	$0{\cdot}007129_5$	$0{\cdot}011163_6$		$0{\cdot}012852_4$
Jones	$0{\cdot}007137_9$	$0{\cdot}011166_7$		$0{\cdot}012856_0$
0·01 *D* KCl (0·745263 g. KCl)				
Parker	0·00077284	$0{\cdot}0012202_3$		$0{\cdot}0014078_9$
Jones	$0{\cdot}0007736_4$	$0{\cdot}0012205_2$		$0{\cdot}0014087_7$

TABLE XXI.-CONSTANTS IN ROBINSON AND STOKES' EQUATION FOR THE EQUIVALENT CONDUCTIVITY OF POTASSIUM CHLORIDE SOLUTIONS AT VARIOUS TEMPERATURES

t°C.	B_1	B_2	B	Λ_0
5	0·2212	$35{\cdot}1_1$	0·3249	94·21
15	0·2249	$46{\cdot}9_8$	0·3267	120·98
25	0·2289	$60{\cdot}3_0$	0·3286	149·80
35	0·2333	$75{\cdot}0_9$	0·3307	180·39
45	0·2381	$91{\cdot}2_1$	0·3330	212·38
55	0·2432	106·8	0·3353	245·73

The specific conductivity of a 0·1 Demal solution over the temperature range 5°–20°C. can be represented by the equation: $k_{0\cdot1D} \times 10^6 = 7137{\cdot}60 + 208{\cdot}312t + 0{\cdot}99077\,t^2 - 0{\cdot}006964\,t^3$, and for a 0·01 Demal solution: $k_{0\cdot1D} \times 10^6 = 773{\cdot}637 + 23{\cdot}0485t + 0{\cdot}110384t^2 - 0{\cdot}0006446\,t^3$.[530] Equivalent conductivity data over the range 100°–300°C. is shown in Table XXII.[531] Measurements of the conductivity by direct current methods are in agreement with the data obtained by the alternating current methods, which have already been quoted.[532] The conductances relative to potassium chloride solution of various 1:1, 1:2, and 2:1 strong electrolytes at very high frequency field strengths (10–200 kV./cm.) have been measured in the course of the investigation of the Wien effect[533] and have been shown to be in agreement with the Onsager-Wilson theory.[534] There is little effect of temperature on these relative conductances.[533] The conductivity of 0·040 M. potassium chloride

TABLE XXII.-EQUIVALENT CONDUCTIVITY OF POTASSIUM CHLORIDE SOLUTIONS AT TEMPERATURES OF 100°C. AND ABOVE

Concentration, M.	100°C.	128°C.	156°C.	218°C.	281°C.	306°C.
0·1000	336·0	415·0	489·5	–	–	–
0·0800	341·5	–	498	638	723	720
0·0100	377·0	470·0	560	741	874	910
0·0020	393·0	–	588	779	930	1008

solution relative to hydrochloric acid increases by 4·2% at 100kV./cm., and 2·4% at 80kV./cm.[535] Very high frequencies have recently been applied in the measurements of electrolytic conductivity of potassium chloride solutions. At 3×10^9 c.p.s. a region of strong dispersion exists at concentrations below 0·5N., owing to the perturbation of the hydration shell of the ions.[536] In a normal solution at 22°C. the conductivity decreases by 5%, when a wave-length of 443cm. is employed in measurement, and by 30% with a wave-length of 23·6cm.[537] The induction heating of potassium chloride solutions by high frequency currents has been investigated.[538]

Increase in pressure results in an increase in the conductance. Measurements have been made at 25°C., up to a pressure of 2700 bars.[539] Data at 30° and 75°C., up to a pressure of 10^4 kg./sq.cm. for a 0·01N. potassium chloride solution are shown in Table XXIII.[540]

TABLE XXIII.-EFFECT OF PRESSURE ON CONDUCTANCE OF POTASSIUM CHLORIDE SOLUTIONS AT 30°AND 75°C.

At 30°C.					
p (kg./sq.cm.)	1	500	1000	1500	2000
Λ_p/Λ_1 (relative conductance)	1·0000	1·0098	1·0100	1·0039	0·9945
	3000	5000	7000	9000	10,000
	0·9582	0·8660	0·7630	0·6646	0·6168
At 75°C.					
p (kg./sq.cm.)	1	500	1500	2500	4000
Λ_p/Λ_1 (relative conductance)	1·0000	0·9878	0·9578	0·9245	0·8670
	6000	8000	10,000	11,000	
	0·7900	0·7150	0·6445	0·6098	

The effect of ultrasonic waves (at 2·8MHz. and 25W.) is to increase the conductivity of potassium chloride solution, the increase becoming larger as the concentration decreases within the range 2M. to 0·01M. After irradiation the solution returns to normal conductivity within 2hr. in the case of the more concentrated solution, and 20hr. in the case of the dilute solution.[541]

In deuterium oxide the electrical conductivity is about 83% of the value in water; data are shown in Table XXIV.[542]

TABLE XXIV.-CONDUCTANCE OF POTASSIUM CHLORIDE IN DEUTERIUM OXIDE-WATER MIXTURES AT 25°C.

Molar Concentration	Mole Fraction n_{D_2O}/n_{H_2O}	Λ
0·04997	0·9935	110·51
0·05007	0·7521	115·33
0·05002	0·4959	120·89
0·04999	0·2471	126·86
0·05000	0·0002	133·37

The Walden product, ($\eta\Lambda$), of equivalent conductivity multiplied by the relative viscosity of the solution, increases in a linear fashion by only 1·93% as the mole ratio of deuterium oxide varies from 0 to 1.[543] The equivalent conductivity at infinite dilution of potassium chloride in deuterium oxide at 18°C. is 105·92; at 21·5°C., 115·13; and at 25°C., 124·54.[544]

The conductivity due to proton mobility of solid aqueous potassium chloride from 0° to −50°C. has been measured. At 0°C. the molar conductivity is 0·1–0·01 mho sq.cm./mole.[545]

The conductivities of aqueous mixed electrolytes have been studied by many investigators as a contribution to our present understanding of these systems. Reference to much of the data on these mixed electrolytes will be made later (see page 1702). The addition of hydrophilic colloids (e.g. gelatin,[546] agar,[547] gum arabic or starch[548]) to potassium chloride solutions reduces the conductivity, the effect being associated with the colloidal viscosity of the solutions.[548] Sucrose and glycerol[549] have a similar effect. However, there is no direct relationship, such as the Walden product, connecting the viscosity and conductance,[550] in fact, the product, $\eta\Lambda$, increases with increasing sucrose concentration.[551] Urea, likewise, decreases the conductivity, but here the Walden product holds,[552] although views to the contrary have been expressed.[553] In aqueous systems containing, in addition to potassium chloride, viscous liquids such as glycerol, ethylpolyglycol, Igepal C, and Dispergal O, it is found that at frequencies of $4{\cdot}39 \times 10^7$,[554] and $8{\cdot}79 \times 10^8$ c.p.s.,[555] the conductivities are not significantly different from those observed at low frequencies. The conductivity increases for 0·1 and 0·001 M. solutions of potassium chloride in glycerol and glycerol-water mixtures when measurements are made at 25°C. with wave-lengths of 23, 46, and 92 m., respectively.[556]

Polarisation phenomena in solutions of potassium chloride at frequencies 13–18,000 c.p.s. and molar concentrations of 10^{-2} to 10^{-4}, have been studied for electrodes of aluminium, nickel, gold, and platinum.[557] Space-charge effects during electrolytic conduction have been described and discussed in terms of potential gradients observed in a column of aqueous potassium chloride solution 40 cm. high, the overall potential difference being 8 V.[558]

There are many difficulties in the determination of the dielectric constant of conducting solutions, and the absolute values for potassium chloride solutions vary considerably. However, despite these variations, a trend in dielectric constant with concentration seems clear. Of the measurements of the dielectric constant, ϵ, many have been made at very high frequencies and most in very dilute solutions.[559-586] A review of data up to 1921 and a bibliography are available.[586] There is general agreement that a plot of ϵ against $\sqrt{c}$ shows a minimum that cannot be reconciled with the simple Debye-Hückel theory. The results, obtained by the resonance method and measured at 8×10^7 c.p.s., given in Table XXV, are among the most recent available.[567] Other data for solutions containing 0–3% of potassium chloride and at 60–110 mc./sec. show only an increase in dielectric constant up to a saturation value between 0·4 and 0·6%;[561] also no minimum has been observed in solutions of concentrations from 0·02–0·06 N. measured at 20°C. and 1000 c.p.s.[568] At 200 c.p.s. the difference between water and a 0·01 N-potassium chloride solution is given as 10%, and as less than 1% for a 0·0001 N. solution.[563] The Drude-Coolidge method at wave-lengths of 1, 2, 3, 4, and 5 m. gives results which agree only qualitatively with the Debye-Falkenhagen theory. The dielectric constant of a potassium chloride solution is stated to be always greater than that of water, the difference decreasing with the frequency and increasing as the square root of the concentration.[564] From the dispersion and absorption of electromagnetic waves of λ = 443 cm., the dielectric constant of water at 22°C. is found to be 79·6, that of 0·035 N-potassium chloride

TABLE XXV.-DIELECTRIC CONSTANTS OF POTASSIUM CHLORIDE SOLUTION AT 25 ± 0·01°C. AT VARIOUS CONCENTRATIONS

Molar concentration	ϵ
0·0000	79·00
0·0002	78·19
0·0005	78·07
0·0010	78·28
0·0025	79·01
0·0040	81·57
0·0050	82·57

82 ± 4; for $\lambda = 23{\cdot}6$ cm., for water $\epsilon = 78{\cdot}2$, and for 0·035 N-potassium chloride $\epsilon = 77 \pm 1$, and for 1·0 N-potassium chloride $\epsilon = 100 \pm 3$.[565] The Drude method employing a wave-length of about 30 m. gives results in the range 0·0005–0·01 N., which are all greater than that found for pure water.[573,574]

The transport numbers of potassium chloride in aqueous solutions have been the subject of numerous investigations over wide ranges of concentration, and at various temperatures. The moving-boundary technique appears to be that most commonly used for the transport number measurements,[587-596] and the method has been compared with that due to Hittorf.[597] Cation transport numbers at 25°C. are shown in Table XXVI.

TABLE XXVI.-CATION TRANSPORT NUMBERS IN POTASSIUM CHLORIDE SOLUTIONS AT 25°C.

Concentration, Molar	Moving-boundary method[592]	Hittorf method[597]
0·001	0·490$_5$	–
0·002	0·490$_4$	–
0·005	0·490$_4$	–
0·01	0·4903	–
0·02	0·4901	0·4893
0·05	0·4899	0·4894
0·1	0·4898	0·4898
0·2	0·489$_2$	–
0·5	–	0·4895
1·0	–	0·4871
3·0	–	0·4859

The data given in Table XXVI have been confirmed and extended.[598] Values obtained by various investigators up to 1931 have been discussed critically.[599] Little difference is observed between the transport number in dilute solution and at a concentration of 4·7 N.[590] At very low concentrations, however, it is reported to be linearly related to the cube root of the dilution,[600] and the variation has been studied in the light of the Onsager and Fuoss equations.[593,602] The majority of the data available refer to 25°C., but some are available for other temperatures and are shown in Table XXVII.[595] The increase in the mobility of potassium ions in the presence of hydrogen ions has been investigated from the view-point of the Debye-Hückel-Onsager theory, using solutions of the salt acidified with hydrochloric acid.[603]

The liquid junction potential of potassium chloride solutions, particularly the saturated solution, with other solutions is of importance in relation to the e.m.f. of cells employing potassium chloride as a salt bridge. Saturated potassium chloride bridges are used to eliminate uncertainties in e.m.f. measurements due to the diffusion potentials, since although two diffusion potentials

TABLE XXVII.- CATION TRANSPORT NUMBERS IN POTASSIUM CHLORIDE SOLUTIONS AT VARIOUS TEMPERATURES

Concentration, Molar	15°C.	25°C.	35°C.	45°C.
0·005	0·4926	0·4903	0·4887	0·4869
0·01	0·4925	0·4902	0·4886	0·4868
0·02	0·4924	0·4901	0·4885	0·4868
0·05	0·4923	0·4900	0·4885	0·4869
0·10	0·4921	0·4900	0·4888	0·4873

instead of one arise, these are usually considerably smaller than the original potential, because the potassium and chloride ions have very nearly the same transport numbers, and the two potentials are often of opposite sign.[603,604] The liquid junction between dilute hydrochloric acid and saturated potassium chloride is 4·7 mV. There is little variation with concentration.[605] The potential between potassium chloride solution and organic liquids such as methyl alcohol, ethyl alcohol, acetone and amyl alcohol is reported as zero.[606] However, in the case of amyl alcohol other workers have reported the existence of a potential difference.[607]

In the electrochemistry of cells employing saturated potassium chloride bridges or potassium chloride solutions in the electrode systems, particular importance attaches to the calomel electrode[608] and cells for the determination of pH, such as $H_2.Pt$ | unknown solution | KCl (saturated) | KCl (0·1 M.) | $[Hg_2Cl_2]$ | Hg,[609] or $H_2.Pt$ | unknown solution | KCl solution | AgCl | Ag.[610] The measurement of the pH of a potassium chloride solution with precision employing a hydrogen electrode is difficult; the value of 6·76 at 25°C.[611] compares well with the value of 6·77, using bromothymol blue as the indicator.[612]

The overvoltage of copper in copper sulphate solution is decreased by the addition of potassium chloride owing to a decrease in the degree of hydration of the copper(II) ion and a resulting decrease in the energy of hydration.[613] The decomposition potential of potassium chloride solution (0·0493 M.) with platinum or iron electrodes is about 2·7 V.[614]

Extensive activity coefficient data of great accuracy are available for potassium chloride solutions over a wide temperature range. The values have been established from e.m.f. measurements,[608,615-621] from vapour pressure data,[622] and from depression of freezing point data.[623,624] A representative selection is shown in Table XXVIII, taken from H. S. Harned and B. B. Owen *loc. cit.* Activity data obtained up to 1925 by the methods enumerated above, have been surveyed.[625,626] Table XXIX gives the values of the activity coefficient obtained by e.m.f. measurements over a wide range of temperatures.[618] The mean activity coefficient of potassium chloride at 100°C. obtained from freezing point data is shown in Table XXX.[627]

Experiments with deuterium oxide show the transport number, t_{K^+}, at 25°C. to be 0·4939 at a potassium chloride concentration of 0·1 molal. From data on the cell: Ag | AgCl | KCl (M. in D_2O) | KCl (M. in D_2O) | AgCl | Ag, the activity of potassium chloride in deuterium oxide is obtained,[629] along with other thermodynamic data. Activity coefficients of potassium chloride solutions have been successfully measured employing an ion exchange resin membrane.[630] The activity coefficient of potassium chloride in the resin phase of various cation[631] and anion[632] exchangers has been investigated. In all cases, the activity in the resin phase was smaller than in the aqueous phase, when the aqueous phase had a low concentration. The ion exchange equilibrium between potassium chloride solution and various ion exchange resins can be considered in terms of the Donnan equilibrium, data on the

TABLE XXVIII.-ACTIVITY COEFFICIENT OF POTASSIUM CHLORIDE DETERMINED BY VARIOUS METHODS

	Temperature 0°C.			
Concentration, Molality	$\gamma_{\pm}$ (e.m.f.)[618,620]	$\gamma_{\pm}$ (e.m.f.)[619]	$\gamma_{\pm}$ (f.p.)[623]	$\gamma_{\pm}$ (f.p.)[624]
0·005	(0·929)		0·929	0·929
0·01	(0·904)		0·903	0·904
0·05	(0·819)		0·818	0·819
0·1	0·768	0·770	0·771	(0·770)
0·2	0·717	0·717	0·719	0·717
0·3	0·683			
0·5	0·642	0·642	0·645	0·644
0·7	0·613	0·615		0·618
1·0	0·588	0·589	0·590	0·588
1·5	0·563	0·562	0·561	
2·0	0·547	0·548		
2·5	0·540	0·541		
3·0	0·539	0·540		
3·5	0·540	0·542		
4·0				

	Temperature 20°C.		Temperature 25°C.	
Concentration, Molality	$\gamma_{\pm}$ e.m.f.[618,620]	$\gamma_{\pm}$ (v.p.)[622]	$\gamma_{\pm}$ e.m.f.[618,620]	$\gamma_{\pm}$ (e.m.f.)[617]
0·005			(0·927)	(0·9275)
0·01			(0·901)	0·902
0·05	(0·816)		(0·815)	0·817
0·1	0·770		0·769	0·770
0·2	0·718	0·721	0·719	0·719
0·3	0·688	—	0·688	—
0·5	0·651	0·651	0·651	0·652
0·7	0·627	—	0·628	—
1·0	0·604	(0·604)	0·606	0·607
1·5	0·582	—	0·585	—
2·0	0·573	0·573	0·576	0·578
2·5	0·568	—	0·572	—
3·0	0·567	0·569	0·573	0·574
3·5	0·571	—	0·574	0·576
4·0	0·574	0·572	0·582	0·581

distribution between resin and potassium chloride solution being available.[633] The diffusion potentials of potassium chloride in ion exchange membranes have been measured. The diffusion velocities follow Fick's Law, and the diffusion constants depend on the exchange capacity and water content of the membrane.[633a]

The thickness of the Helmholtz double layer formed on two gold electrodes in potassium chloride solution is 0·194 × 10^{-6} cm. at a concentration of 0·1N., and 0·325 × 10^{-6} cm. at 0·001N.[634] The electrocapillary curves for mercury at 25°C. with a range of potassium chloride solutions show maxima as indicated in Table XXXI.[635]

Electrokinetic phenomena (zeta potentials) have been investigated with potassium chloride solutions for quartz powder,[636,637] Jena glass capillaries,[638] Pyrex glass powder,[639] various textile fibres,[640] and cellulose.[641] Surface conductivity has been invoked to explain abnormal electrokinetic potentials.[642]

TABLE XXIX.-MEAN ACTIVITY COEFFICIENTS OF POTASSIUM CHLORIDE AT VARIOUS TEMPERATURES

Concentration, Molality	0°C.	5°C.	10°C.	15°C.	20°C.	25°C.	30°C.	35°C.	40°C.
0·1	0·768	0·769	0·769	0·769	0·770	0·769	0·768	0·767	0·765
0·2	0·717	0·718	0·718	0·719	0·718	0·719	0·718	0·717	0·715
0·3	0·683	0·685	0·687	0·687	0·688	0·688	0·687	0·685	0·682
0·5	0·642	0·646	0·648	0·650	0·651	0·651	0·651	0·648	0·646
0·7	0·613	0·619	0·623	0·624	0·627	0·628	0·629	0·627	0·626
1·0	0·588	0·595	0·598	0·601	0·604	0·606	0·604	0·604	0·603
1·5	0·563	0·570	0·576	0·579	0·582	0·585	0·585	0·585	0·585
2·0	0·547	0·554	0·562	0·568	0·573	0·576	0·578	0·579	0·578
2·5	0·540	0·549	0·556	0·562	0·568	0·572	0·574	0·575	0·575
3·0	0·539	0·549	0·556	0·562	0·567	0·571	0·573	0·574	0·573
3·5	0·540	0·550	0·558	0·565	0·571	0·574	0·577	0·578	0·578
4·0	—	—	0·563	0·569	0·574	0·579	0·582	0·584	0·585

TABLE XXX.-ACTIVITY COEFFICIENT OF POTASSIUM CHLORIDE AT 100°C. (FROM BOILING POINT ELEVATION DATA)

Concentration, Molality	$\gamma_\pm$	Concentration, Molality	$\gamma_\pm$	Concentration, Molality	$\gamma_\pm$
0·001	0·959	1·0	0·566	4·5	0·562
0·005	0·914	1·5	0·551	5·0	0·569
0·01	0·884	2·0	0·545	5·5	0·576
0·05	0·786	2·5	0·545	6·0	0·583
0·1	0·732	3·0	0·547	6·5	0·590
0·2	0·676	3·5	0·551	7·0	0·598
0·5	0·600	4·0	0·556	7·5	0·606

TABLE XXXI.-ELECTROCAPILLARY MAXIMA IN POTASSIUM CHLORIDE SOLUTIONS

Normality	$-E$ (± 5 mV.)	γ (dynes/cm.)
3·0	575	421·8
1·0	550	424·2
0·3	550	425·2
0·1	560	426·2
0·03	575	426·5
0·01	610	426·8

For aqueous 0·001 N-potassium chloride solution at 25°C., the extra conductivity near optically polished glass, fused silica and optically polished quartz amounts to a surface conductivity of $4·3 \times 10^{-8}$ mhos.[643] The surface conductivity at the interface between fritted Pyrex glass and 0·0005 N-potassium chloride solution is independent of the frequency and intensity of the current, but varies greatly with time and with the method used for cleaning the surface.[644]

Electro-osmosis of potassium chloride solution with parchment,[645] silica gel,[646] Pyrex glass,[647] and ceramic[648] diaphragms has been observed and measured. The transport of potassium chloride through membranes of cellophane,[649] chromated gelatin, parchment, parchment paper, and collodion,[649,650] has been treated quantitatively. Transport number measurements with parchment membranes indicate values of 4 and 5 as the hydration numbers of the chloride and potassium ions, respectively.[651] The electro-osmosis of 0·02 N-potassium chloride solution through a slit formed by two thin plates of glass,

$10 \times 1{\cdot}55$ cm. in size and set 5×10^{-2} mm. apart, is found to agree with osmosis observed using powdered glass.[652] The surface capacity of mercury in contact with aqueous potassium chloride has been measured.[653]

Information on the diffusion of potassium chloride in aqueous solutions has been considerably extended beyond that given in Mellor, II, 548. Table XXXII gives a selection of data.

TABLE XXXII.-DIFFUSION CONSTANTS FOR POTASSIUM CHLORIDE SOLUTIONS AT VARIOUS TEMPERATURES

Concentration	Diffusion constant $\times 10^5$ cm.^{2} sec.$^{-1}$	Temperature	Method	Reference
2%	$1{\cdot}75_5 \pm 0{\cdot}02$	22·6	Interferometry	654
0·00125 M.	1·9612	25	Conductance	655
0·00194 M.	1·9545	25	Conductance	655
0·00325 M.	1·9433	25	Conductance	655
0·00585 M.	1·9308	25	Conductance	655
0·00704 M.	1·9241	25	Conductance	655
0·00980 M.	1·9180	25	Conductance	655
0·1 M.	$1{\cdot}851_2$	25	Gouy-interference	656
0·5 M.	$1{\cdot}849_7$	25	Gouy-interference	656
1·0 M.	$1{\cdot}892_3$	25	Gouy-interference	656
2·0 M.	$1{\cdot}999_4$	25	Gouy-interference	656
3·0 M.	$2{\cdot}112_0$	25	Gouy-interference	656
3·9 M.	$2{\cdot}195_6$	25	Gouy-interference	656
0·5 N.	1·22*	17	Internal precipitant	657
Saturated Solution	2·107	17·3	–	658

* Measured in gel

The integral diffusion coefficient, $\bar{D}^0_{(c)}$, for a run of vanishingly short duration between concentration, c, and pure water, is related to the true differential coefficient by the expression:

$$\bar{D}^0_{(c)} = \frac{1}{c}\int_0^c D\,dc$$

Data for $\bar{D}^0$ in cm.^{2} sec.$^{-1}$ $\times 10^{-5}$ at 25°C. are as follows:[659]

Concentration, moles/litre	$\bar{D}^0$
0·000	1·996
0·001	1·794
0·002	1·966
0·003	1·960
0·005	1·951
0·007	1·945
0·01	1·938
0·02	0·920
0·03	1·908
0·05	1·893
0·07	1·883
0·1	1·873
0·2	1·857
0·3	1·850
0·5	1·848

continued on following page

Concentration, moles/litre	$\bar{D}^0$
0·7	1·851
1·0	1·859
1·2	1·866
1·4	1·874
1·6	1·882
1·8	1·892
2·0	1·901
2·5	1·927
3·0	1·953
3·5	1·979
3·9	2·000

The diffusion coefficient data[660] fit the Onsager-Fuoss diffusion equation.[661] The diffusion of potassium chloride into hydrochloric acid at 10°C.[662] and at 25°C.[663] has been measured. The diffusion of a 0·02 N-potassium chloride solution through sand saturated with water was measured by a conductivity method, the average diffusion found being 1·6 mm. per day.[664] Diffusion of potassium chloride out of single capillaries, from tubes containing beds of small glass beads, and from porous alumina spheres, has been studied.[665] In the diffusion of a mixture of potassium chloride and potassium sulphate in agar gel at 10°–20°C., the diffusion coefficient of the potassium chloride is reported to be greater than when diffusing alone in the gel under comparable conditions.[666] With a specimen of a 3% gelatin gel containing thermolysed gelatin, the diffusion is more rapid than that with a simple gelatin gel.[667] The Soret effect, which is the slow development of a concentration gradient in a homogeneous solution subjected to a vertical temperature gradient, has been studied with potassium chloride solution. The Soret coefficient, diffusion constant, and thermal diffusion coefficient, measured using a flat cylindrical cell of variable height, *h*, under a temperature gradient of from 25°C. to 35°C., are given in Table XXXIII.[668]

TABLE XXXIII.-SORET COEFFICIENTS, DIFFUSION, AND THERMAL DIFFUSION CONSTANTS FOR POTASSIUM CHLORIDE SOLUTIONS

Mole fraction	Soret coefficient	Diffusion constant cm.^{4}/sec. × 10^5	Thermal diffusion constant cm.^{2}/sec./deg. × 10^5
Height of cell = 0·695 cm.			
0·01826	−0·51 × 10^{-3}	1·12	−0·57 × 10^{-3}
0·03692	−0·72 × 10^{-3}	1·30	−0·99 × 10^{-3}
0·05067	−0·91 × 10^{-3}	1·90	−1·73 × 10^{-3}
0·07458	−1·23 × 10^{-3}	1·38	−1·70 × 10^{-3}
Height of cell = 0·975 cm.			
0·01826	−0·27 × 10^{-3}	3·04	−0·82 × 10^{-3}
0·03692	−0·76 × 10^{-3}	1·52	−1·16 × 10^{-3}
0·05067	−0·97 × 10^{-3}	1·92	−1·86 × 10^{-3}
0·07458	−1·07 × 10^{-3}	2·64	−2·18 × 10^{-3}

The Soret coefficient has also been measured using a fine glass frit,[669] or a permeable membrane,[670] and by a thermoelectrical method.[671] From experiments with a vertical column, the Soret coefficient of 0·05 N-potassium chloride solution at 30°C. is 1·20 × 10^{-3}; at 40°C., 2·26 × 10^{-3}; at 50°C., 2·77 × 10^{-3}; and at 60°C., 3·18 × 10^{-3} sec.$^{-1}$.[672]

A very large amount of work has been done on the coagulation of colloids by electrolytes using potassium chloride. The results are in no way specific to potassium chloride and no further reference to it will be made here.

Potassium chloride restores thixotropic properties to electrodialysed bentonite.[674] The adsorption of electrolytes from aqueous solutions by materials such as charcoal from various sources,[675] barium sulphate,[676] carborandum,[677] metallic silver and gold,[678] copper ferrocyanide[679] and silica,[680] has been studied employing potassium chloride solutions.

Under the action of ultrasonic radiation at 400 kc./sec. and at 1·0 Mc./sec. hydrogen peroxide is produced in dilute oxygenated solutions of potassium chloride, but in quantities little different from those formed in pure water under similar conditions.[681],[682] An ultrasonic interferometric method has been described by means of which the volume of hydration water of potassium chloride solutions may be calculated on the basic assumptions that the ions of the salt and the hydrated water are incompressible, and that the observed decrease in compressibility resulting from the solution process and from increase in concentration is due to hydrate formation.[683–685] The absorption of ultrasonic energy by aqueous solutions of potassium chloride of concentrations up to 0·6 N. at various frequencies has been studied.[686] The Debye effect in solutions of the salt, as caused by sustained sinusoidal ultrasonic excitation,[687] or by pulse trains,[688] has been detected and measured. It is recorded that anomalous values are observed for the velocity of ultrasonic radiations at 0·625–2·5 Mc./sec. in 1–6% solutions of potassium chloride at 24°C., this being the dilution range over which so-called negative viscosity effects appear.[689] More recently, however, other investigators have reported that at 25°C. and at 3·0[690] and 6·4 Mc./sec.,[691] the velocity is an uninterruptedly linear function of concentration for solutions containing up to 15% of the salt.[690] Variations of electrical conductivity occurring simultaneously with those of adiabatic compression in irradiated solutions of potassium chloride have been measured, and the results have been applied to the calculation of the pressure and temperature coefficients of conductivity with the aid of Onsager's equation. For a 0·0001 N. solution at 25°C., the magnitude of the two side band voltages, as calculated from measurements of electrical conductivity with a.c., is about 53 μV./atm. acoustic pressure/V. applied.[692] Ultrasonic pulse-trains at a carrier frequency of 200 kc./sec. have been used for the generation of alternating potential gradients in solutions of potassium chloride. In a 0·001 N. solution, the ionic vibration potential is 6 μV. per cm./sec., from which it has been calculated that there is a difference of 80 between the apparent gramionic-masses of the hydrated anions and cations of the solute.[693] The velocity of ultrasonic radiation in concentrated solutions of potassium chloride at frequencies and temperatures of 0·47–12·87 Mc./sec., and 15°–55°C., respectively, has been measured.[694] No dispersion occurs under these conditions.[694] For a 20% solution of the salt, the velocity is 1632·5, 1643·3 and 1643·7 m./sec. at temperatures of 19·8°, 26·6°, and 26·7°C., respectively, at 0·5 Mc./sec.[695]

Aqueous systems containing potassium chloride and other components.

A considerable number of systems of this type have been investigated. The information which follows contains only items referring to phase diagrams and such physical properties as are considered of importance. Many of the systems are of technological interest. In Table XXXIV ternary systems based on potassium chloride-water and one other component are listed. The properties of solutions containing potassium chloride and sugars, particularly sucrose, are reported in some detail. Reference has already been made to the electrical conductivity (*vide supra*) of solutions containing potassium chloride and sucrose. Data are also available for the heats of dilution,[834] viscosity at 20°, 30°, 40°, and 60°C.,[835] and activities[836] in these solutions. The solubility curve at 30°C. of the ternary system KCl-sucrose-water shows

TABLE XXXIV.-AQUEOUS TERNARY SYSTEMS CONTAINING POTASSIUM CHLORIDE

Additional Component	Data
HCl	Electrical conductivities;[696,697] Viscosities;[697] e.m.f. measurements of activities.[698]
LiCl	Transport numbers;[699] activity coefficients;[700] vapour pressures;[701] electrical conductivities at 25°C.[702]
NaCl	Transport numbers;[703] electrical conductivities at 25°C.;[704] viscosities and densities at 25°, 40°, and 60°C.;[705] phase diagram;[706-708,347] phase diagram 100°–230°C.;[346] phase diagram −23° to +190°C.;[709] solubilities at 15°C.;[710] solubilities up to 111·3°C.;[711] solubilities at 25°–100°C.;[757] solubilities of solutions saturated with NaCl;[712] calculation of solubility diagram at 25°C.;[713] activity coefficients;[714] crystallisation at 300°–650°C. under a pressure of 300–350 atm.;[715] Faraday effect;[716] electrokinetic potential ;[717] surface tension;[718] densities and refractive indices at 20°C.[719]
NaN_3	Electrical conductivities.[720]
Na_2CO_3	Phase diagram at 25°C.[721]
$Na_2Cr_2O_7$	Phase diagram.[722]
$NaNO_3$	Cryoscopic measurements;[724] equilibrium system.[706,725]
$NaClO_4$	Phase diagram at 25°C.[726]
Na_2SO_4	Equilibrium diagram at 0°, 25°, 50° and 75°C.[727]
$Na_2SO_4,10H_2O$	Cryoscopic measurements.[728]
KF and KHF_2	Phase diagram at 25° and 75°C.[729]
KBr	Phase diagram;[707] phase diagram −13·4° to +30°C.;[730] phase diagram at 25°C.;[731] phase diagram at 35°C.;[732] solubilities, densities and optical properties of crystalline phases;[733] Faraday effect;[716] composition of solid phase plotted against temperature of deposition.[734]
$KClO_3$	Solubilities at 20°, 25°, 50°, and 75°C.[735]
K_2CO_3	Phase diagram.[736]
$KHCO_3$	Phase diagram 10°–40°C.[737]
$K_2Cr_2O_7$	Solubilities at 20°, 25°, 30°, and 40°C.;[738] effect of agar on crystallisation.[739]
KOH	Phase diagram;[740] e.m.f. measurement of activities.[698]
KIO_3	Phase diagram at 5°, 25°, and 50°C.[741]
KNO_3	Phase diagram;[742] phase equilibria at 30°C.[743]
KNO_2	Equilibria at 0°, 20°, 40°, 60°, and 98°C.[744]
$K_2C_2O_4$	Equilibrium at 20°C.[745]
$KReO_4$	Phase diagram at 0° and 30°C.[746]
KH_2PO_4	Phase diagram at −10·8° to +35°C.;[747] phase diagram at 0°, 25°, and 50°C.;[748] phase diagram at 0°C.[749]

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TABLE XXXIV.-CONTINUED

Additional Component	Data
KSO_3NH_2	Phase diagram at 25°C.[750]
K_2SO_4	Phase diagram at 30°C.[751]
$KHSO_4$	Solubility at 20°C.[752]
α-KCNS	Vapour pressure.[753]
RbCl	Solubility system at 25°C.[754]
RbBr	Phase diagram at 25°C.[755]
CsCl	Isopiestic measurements at 25°C.[756]
$MgCl_2$	Solubility, density, and optical properties of solid phases;[733] solubilities at 25° and 100°C.;[757] solubilities at 15·4° and 90°C.;[758] solubility at 35°C.;[759] empirical formula governing solubility;[760] phase diagram at 0°C.;[761] comparison with $NaCl-MgCl_2-H_2O$ system;[762] thermodynamic study by an isopiestic method;[763] heat of solution at 50° and 66°C.;[764] electrical conductivities;[765] densities and refractive indices at 20°C.;[719] viscosities, densities, and refractive indices.[766]
$Mg(OH)_2$	Solubilities at 25°C. of components are independent of one another.[767]
$Mg(NO_3)_2$	Phase diagram at 25°C.[768]
$MgSO_4$	Phase diagram at 25°C.;[769] phase diagrams at 15°, 25°, 35°, and 55°C.;[770] solubilities at 25°C.;[771] heat of solutions at 50° and 66°C.;[764] electrical conductivities.[720]
$CaCl_2$	Phase diagram at 0°C.;[761] phase diagram at 30° C.;[743] phase diagram at 35°C.;[759] freezing point of KCl in $CaCl_2,6H_2O$.[772]
$Ca(ClO_3)_2$	Equilibria at 15° and 45°C.;[773] isotherms at −10°, 0°, and +25°C.[774]
$Ca(NO_3)_2$	Phase diagram at 30°C.[743]
CaC_2O_4	Solubility in KCl.[775]
$Ca(HPO_4),2H_2O$	Solubility in KCl at 40°C.[776]
$CaSO_4$	Solubility at 55°C.;[777] solubility at 25°C.[778]
$SrCl_2$	Heat of dilution, evidence for K_2SrCl_4;[779] phase diagram.[780]
$BaCl_2$	Thermodynamic study by isopiestic method;[763] interfacial tension in contact with butyl alcohol;[781] specific refractivities of system;[782] system;[783] densities and refractive indices at 21 ± 0·03°C.;[784] electrical conductivities and freezing point depressions.[785]
$LaCl_3$	Electrical conductivity.[786]
$CeCl_3$	Phase diagram at 30°C.[787]
Mn(II), Co(II), Ni(II), and Cu(II) chlorides	Thermodynamic studies by an isopiestic method.[763]
$CoCl_2$	Interfacial tension in contact with *iso*-amyl acetate;[788] phase diagram at 20°C,;[789] phase diagram;[790] phase diagrams at 0°, 38°, 50°, 51°, 75°, and 100°C.[791]
$CoSO_4$	Equilibrium isotherms at 0°, 38°, 50°, 75°, and 100°C.;[791,792] isotherm at 25°C.[793]

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TABLE XXXIV.-CONTINUED

Additional Component	Data
$FeCl_3$	System at 0°, 25°, 31°, and 60°C.;[794] system;[795] compressibilities from ultrasonic measurements.[796]
$CuCl_2$	Interfacial tension in contact with butyl acetate;[797] system at −65° to +121·5°C.[798]
$Cu(IO_3)_2$	Solubility.[799]
AgCl	Solubility.[800]
$CdCl_2$	System;[801] equilibrium isotherms from −10° to +100° C.;[802] refractive indices at 20°C.;[803] ebullioscopic study.[804]
$HgCl_2$	System at 25°C.;[805] interfacial tension in contact with butyl acetate;[806] ebullioscopic study;[807] spectroscopic study.[808]
$Hg(CN)_2$	Ebullioscopic study.[809]
$AlCl_3$	System at 25°C.;[810] system at 0°, 40°, 60°, and 80°C.[811]
$Al(NO_3)_3$	System at 0° and 10°C.[812]
$PbCl_2$	Vapour pressure at 25°C.;[813] activities;[814] thermodynamics of system at 25°C.;[815] system at 25°C.[816]
NH_4Cl	Equilibrium system at 30°C.,[817] system at 20°C.;[818] solubility equilibrium and densities at 0°, 25°, 45°, 65°, and 90°C.;[819] solubility isotherms at 0°, 20°, 40°, and 60°C.[820]
NH_4NO_3	System at 0°C.;[820] system at 100°C.;[821] solubility equilibrium at −10° and −15°C.;[822] boiling point of system;[823] phase diagram −20° to +30°C.[824]
$(NH_4)_2SO_4$	System at 20°C.;[825] system at 25°C.[826]
$(NH_4)H_2PO_4$	System at 0°C.[827,749]
SO_2	Solubility up to a KCl concentration of 30 g. per 100 g. water, from 10° to 90°C.[828]
K oleate	System up to 210°C. (salting out of soap).[829]
K laurate	System up to 225°C.[830]
K benzoate	Absorption spectra suggest complex formation.[831]
Urea	Phase diagram;[832] solubility equilibrium −19·4° to +40°C.[833]

no compounds to be formed.[837] This system is of importance in the sugar industry, and viscosity data are available.[838] Examination of systems containing, in addition, other sugars such as ∂-glucose and ∂-fructose, shows that the solubility of sucrose is decreased as compared with the simple ternary system of sucrose-KCl-water.[839] The phase diagrams for the quaternary systems sucrose-fructose-KCl-water, sucrose-glucose-KCl-water and glucose-fructose-KCl-water[840] at 30°C. are reported, and for the quinary system sucrose-glucose-fructose-KCl-water.[841] The phase equilibrium of the system glucose-KCl-water at 10°–20°C. shows no evidence of compound formation.[842]

In Table XXXV poly-component systems based on potassium chloride-water and other components are listed.

Solutions of Potassium Chloride in Non-Aqueous and Mixed Solvents.

The solubility of potassium chloride in liquid hydrogen cyanide at 0°C. is 0·10 mole/l., with a corresponding conductivity of 0·0085 mho/cm., which is about 0·005 of the value in water.[870] At 18°C., the equivalent conductivity of such a solution is given by the expression: $\Lambda_c = 363{\cdot}4 - 280\sqrt{c}$, where

TABLE XXXV.-AQUEOUS POLY-COMPONENT SYSTEMS CONTAINING POTASSIUM CHLORIDE

System	Data
$K^+, Na^+, Cl^-, Br^-, I^-$,	Distribution of I and Br between solid and solution.[843]
$K^+, Na^+, Cl^-, NO_3^-, SO_4^{2-}$	Phase diagram 0°–90°C.[844]
$KCl, NaCl, NaBr(KBr)$	System studied by isothermal evaporation.[845]
$KCl, NaCl, HCl$	Empirical equation governing solubility relationships.[846]
$KCl, NaCl, MgCl_2$	System at 125°, 150°, 200°, and 265° C.;[847] representation of system discussed;[848] heat capacity;[849] system at 25°C.;[754] system at 25° and 100°C.;[757] vapour pressure;[850] kinetic determination of solution equilibrium.[851]
$KCl, NaCl, MgCl_2, FeCl_2$	Isotherm at 55°C.[852]
$MgCl_2, MgSO_4$	System;[853] system at 15°, 25°, 35°, and 55°C.[770]
$K^+, Na^+, Mg^+, Cl^-, NO_3^-$	Equilibria in system 0°–80°C.[854]
$KCl, NaBr, MgSO_4$	Electrical conductivity.[720]
$K^+, Na^+, NH_4^+, Cl^-, HCO_3^-$	System.[855]
$K^+, Na^+, Cl^-, SO_4^{2-}, NH_3$	Equilibrium.[856]
$KCl, NaCl, NH_4Cl$	Refractive index at 15°C.[710]
K^+, Cl^-, Br^-, I^-	Distribution of I and Br between solid and solution.[843]
$KCl, KBr, MgCl_2, MgBr_2$	System at 20°C.[857]
$KCl, K_2Cr_2O_7, KNO_3$	Solubility from 40°C. to complete solidification.[858]
KCl, KNO_3, K_2SO_4	Equilibria at 25°C.[859]
KCl, K_2CO_3, K_2SO_4	Solubilities at 10°, 25°, and 40°C.[860]
$KCl, K_2SO_4, MgSO_4$	Solubility in system at 24°C.[861]
$KCl, RbCl, MgCl_2$	System at 25°C.;[857] solubility isotherms at 100°C.[862]
$KCl, RbCl, NH_4Cl$	Phase system at 25°C.[857]
$KCl, MgCl_2, FeCl_3$	Solubilities.[795]
$KCl, CaCl_2, SrCl_2$	Equilibria in system at 18°–114°C.[863]
$KCl, FeCl_3, AlCl_3, HCl$	System at 25°C.[864]
$KCl, AlCl_3, HCl$	System at 25°C.[865]
K^+, Al^{3+}, H^+, Cl^-	System.[866]
$KCl, HgCl_2, NH_4Cl$	System at 25°C.[857]
$KCl, SbCl_3, HCl$	Complex salts formed.[867]
$K^+, NH_4^+, Cl^-, NO_3^-, H_2PO_4^-$	Phase study.[868]
$KCl, (NH_4)_2SO_4, NH_4OH$	System at 25°C.[826]
KCl, NH_4NO_3, NH_4OH	Isotherms at −10°, +20°, and +40° C.[869]

c is the concentration in gram equivalents per litre of solution.[871]

The solubilities of potassium chloride measured in water-hydrogen peroxide mixtures (0–100 mole%) at 0°, 15°, and 25°C., show that whilst at high hydrogen peroxide concentrations the temperature dependence is small, with solvents rich in water an appreciable temperature dependence exists. The solubilities in hydrogen peroxide mixtures are greater than in water alone; this is also true of sodium fluoride and potassium nitrate, but not of sodium chloride, sodium nitrate, or lithium nitrate, for which the reverse holds.[872] The solubilities at 25°C. in hydrogen peroxide-water mixtures are shown in Table XXXVI.[873]

TABLE XXXVI.-SOLUBILITY (MOLE/LITRE OF SOLUTION) OF POTASSIUM CHLORIDE IN HYDROGEN PEROXIDE-WATER MIXTURES AT 25°C.

Mole fraction H_2O_2	Solubility
0·0000	4·826
0·0288	4·835
0·0599	4·974
0·0899	5·093
0·1270	5·263
0·1585	5·362
0·1955	5·534

The relation of electrical conductivity and dilution of potassium chloride in hydrogen peroxide-water mixtures is very similar to that for solutions in water. Selected data for conductivity are given in Table XXXVII.[874]

TABLE XXXVII.-ELECTRICAL CONDUCTIVITY OF POTASSIUM CHLORIDE IN HYDROGEN PEROXIDE-WATER MIXTURES AT 0°C.

% H_2O_2	Dilution in litres	Specific Conductivity $ohm^{-1}cm.^{-1}$
22·26	0·500	9·62 × 10^{-2}
	1·020	5·36 × 10^{-2}
	5·000	1·26 × 10^{-2}
	50·0	1·41 × 10^{-3}
	100·0	7·63 × 10^{-4}
35·48	1·10	4·84 × 10^{-2}
	10·10	5·88 × 10^{-3}
	107·3	6·30 × 10^{-4}
90·2	1·016	5·00 × 10^{-2}
	9·083	6·15 × 10^{-3}
	82·10	7·73 × 10^{-4}
100	0·995	4·51 × 10^{-6}
	11·1	5·11 × 10^{-3}
	123·0	6·12 × 10^{-4}

In liquid ammonia, the solubility of potassium chloride is 5, 4, 3, 2, and 1·5 g./1000 g. of ammonia at −50°, −25°, 0°, 25°, and 50°C., respectively;[875] other investigators report a solubility of 0·213 g./100 g. of ammonia at −33·9° C.;[876] 0·132 g./100 g. of solution at 0°C.;[877] and 0·04 g./100 g. of ammonia at 25°C.[878] The activity of potassium chloride at 35°C. in liquid ammonia has been obtained from e.m.f. measurements.[879]

The equivalent conductivity of potassium chloride in anhydrous hydrazine at 25° and 0°C. is 130·3 and 86·2, respectively, at infinite dilution. Data at other concentrations are given by the equations: $\Lambda_{25} = 130{\cdot}3 - 145\sqrt{c}$, and $\Lambda_0 = 86{\cdot}2 - 89\sqrt{c}$.[880]

The solubility in phosphorus oxychloride at 25°C. is 0·60 g./l., and the corresponding electrical conductivity, 3·4 × 10^{-5} $ohm^{-1}cm.^{-1}$.[881] The use of a 0·1 M. potassium chloride reference electrode in selenium oxychloride solutions is reported. Potassium chloride is a base in this system.[882] It is insoluble in liquid nitrosyl chloride[883] and in cyanogen chloride.[884]

The solubilities in methyl alcohol-water mixtures at 25°C. are given in Table XXXVIII.[873]

TABLE XXXVIII.-SOLUBILITY OF POTASSIUM CHLORIDE IN METHYL ALCOHOL-WATER MIXTURES AT 25°C.

Weight % Methyl alcohol	Mole fraction Methyl alcohol	Solubility, mole/1000 g. solution
11·10	0·0656	3·638
20·11	0·1240	2·820
29·87	0·1933	2·077
39·93	0·2721	1·476
50·65	0·3661	0·9561
59·28	0·4502	0·6487
69·74	0·5645	0·3766
78·98	0·6787	0·2193
80·45	0·6983	0·2005
90·04	0·8248	0·1135
100·00	1·000	0·0707

Data at 10·2° and 19·9°C. are shown in Table XXXIX.[885]

TABLE XXXIX.-SOLUBILITY OF POTASSIUM CHLORIDE IN METHYL ALCOHOL-WATER MIXTURES AT 10·2° AND 19·9°C.

Methyl alcohol %	Solubility at 10·2°C. mole/l. solution	Solubility at 19·9°C. mole/l. solution
25·96	1·700	1·896
45·13	0·8403	0·8700
74·88	0·1886	0·212
100·00	0·0520	0·0560

The ratios of the solubility of potassium chloride at various temperatures up to 100°C. in water, to that in aqueous methyl alcohol of various compositions, are reported.[886] In anhydrous methyl alcohol, various investigators report the solubility of potassium chloride as 0·49 and 0·53 g./100 g. at 18° and 25°C., respectively;[887] 4·28 g./l. at 10°C.;[888] 0·00833, 0·00729, 0·00691, 0·00642, 0·00528, and 0·00415 moles of potassium chloride per mole at 20°, 30°, 35°, 40°, 45°, and 50°C., respectively.[889] The densities and viscosities of potassium chloride dissolved in methyl alcohol at 25°C., measured over a wide range of concentrations, are given by the equations: $d_4^{25} = 0{\cdot}786545 + 0{\cdot}067895\,c$ and $\eta = 1 + 0{\cdot}00367\sqrt{c} + 0{\cdot}43974\,c - 0{\cdot}21803\,c \log c$.[890] Potassium chloride is, however, reported to show a negative viscosity in methyl alcohol which is not in accord with the above equation,[891] nor with an isolated measurement at 25°C., which gives the absolute viscosity of a potassium chloride solution containing 0·04713 mole/1000 g. of solution, as 0·00565.[892] A number of investigations cover the electrical conductivity of potassium chloride in anhydrous methyl alcohol[893,894] and aqueous methyl alcohol.[895,896] In anhydrous methyl alcohol the equivalent conductivity at 25°C. is given by the equation: $\Lambda_0 = 104{\cdot}78 + 1005\,c + 375\,c \log c$, where c is the concentration in moles per litre. Density data are also given.[893] The activity coefficient at 25°C. of potassium chloride in water-methyl alcohol mixtures has been obtained by e.m.f. measurements.[897] Transport numbers in anhydrous methyl alcohol at 25°C. have been measured by the moving boundary method, using potassium chloride solutions of 0·005 N. to 0·02 N. The cationic transference number at zero concentration is 0·5001.[898] The heat of solution in methyl alcohol at 0·0122 M. is −1·41 kg.-cal. per mole, the heat of transference from methyl alcohol to water being +2·94 kg.-cal. per mole.[899] The solubilities of potassium chloride in methyl alcohol, ethyl alcohol, acetone, and ether, have been tabulated. Errors are often introduced in extraction analysis by ignoring this solubility.[900]

The solubility data for potassium chloride in ethyl alcohol reported in Mellor, II, 543, have been extended by measurements in the anhydrous solvent at various temperatures, as shown in Table XL.[889]

TABLE XL.-SOLUBILITY OF POTASSIUM CHLORIDE IN VARIOUS ALCOHOLS AT TEMPERATURES FROM 20°–50°C. (MILLIMOLES/MOLE SOLVENT)

Temperature, °C.	Ethanol	*n*-Propanol	*iso*Propanol	*n*-Butanol	*iso*Butanol
20	1·270	0·0700	1·235	0·0822	0·0326
30	1·378	0·0796	1·300	0·0852	0·0356
35	1·443	0·0793	1·340	–	–
40	1·454	0·00773	1·390	0·0904	0·0400
45	1·277	0·00683	1·295	–	–
50	0·845	0·00473	1·060	0·0925	0·0407

The solubilities of potassium chloride in solutions of ammonium nitrate in ethyl alcohol show deviations from the Debye-Hückel theory, but with a modified treatment of the interionic forces, the results can be shown to agree at least qualitatively.[901] Evidence based on activity data suggests that there is no solvation of potassium chloride in ethyl alcohol-water solutions.[902] Potassium chloride in ethyl and propyl alcohols is reported to show a negative temperature coefficient of viscosity.[891] The surface tension of 0·99 molal potassium chloride in 2·03 mole% aqueous methyl alcohol is 54·45 dynes/cm.; for a 1·99 *m.* solution, 53·08; for 2·98 *m.*, 52·01; and for 3·97 *m.*, 51·51.[903] Various aspects of 'salting out' have been studied using aqueous ethyl alcoholic solutions of potassium chloride, primarily from the viewpoint of the heats of solution of potassium chloride in this solvent.[904] Solutions of potassium chloride in 50% aqueous ethyl alcohol at 10°C. dissolve more of certain organic compounds, such as benzene, carbon tetrachloride, and methyl salicylate, than does a simple 50% aqueous ethyl alcohol; this effect is known as 'salting in'.[905] The electrical conductivity of potassium chloride in aqueous ethyl alcohol indicates complete dissociation.[896] Mixed crystals of rubidium and potassium chlorides are formed when an alcoholic solution of these salts is saturated with hydrochloric acid.[906] The ternary system KCl-KBr-50% aqueous ethanol is a Roozeboom Type II system.[907] A compound of the formula $5KCl,6HgCl_2\ 2EtOH$ is reported to be obtained from the system KCl-$HgCl_2$-EtOH studied at 34°C.[908] The ternary systems KCl-H_2O-propyl alcohol at 25°C.,[909,910] and KCl-H_2O-*tert.*-butyl alcohol at 30°C.,[911] have been studied. The solubilities of potassium chloride in anhydrous *iso*- and *n*-propyl and butyl alcohols at various temperatures are given in Table XL.[889] Conductivities of potassium chloride, measured in *iso*propyl alcohol-water mixtures, are in accord with current electrolyte theory.[896,912] The conductivity of potassium chloride in glycerol at 25°C. is related to the water content and can, in fact, be applied to determine the moisture content.[913] The solubility of potassium chloride in ethylene glycol is given in Table XLI.[914] The system KCl-allyl alcohol-water, which has two critical solution points, is reported.[910]

The solubility of potassium chloride in anhydrous formic acid at 18° and 25°C., is 19·1 and 19·2 g./100 g. solvent, respectively.[887] The equivalent conductivity at infinite dilution of potassium chloride in anhydrous formic acid at 8·50°C. is 35·8.[915] The solubility in anhydrous acetic acid is given in Table XLII.[916] The surface tension of a 1·018 molal solution of potassium chloride in 0·353 mole% aqueous acetic acid is 69·49 dynes/cm.; in a 2·037 *m.* solution, it is 70·43; in 3·056 *m.*, 71·30; and in 4·074 *m.*, 72·31.[903]

The system KCl-acetone-water, which has two critical solution points, TABLE XLI.-SOLUBILITY OF POTASSIUM CHLORIDE IN ETHYLENE GLYCOL AT 30°C.

% Glycol	g.KCl/100 g. solvent
0·00	37·18
19·33	28·16
40·10	19·80
58·98	13·43
79·42	8·40
100·00	5·37

TABLE XLII.-SOLUBILITY OF POTASSIUM CHLORIDE IN ANHYDROUS ACETIC ACID (MOLE PERCENTAGE OF SOLUTE)

Temperature, °C.	Solubility
24	0·157
30	0·170
39	0·188
47	0·207
55	0·229
59	0·239
63	0·257
70	0·272
76	0·295
87	0·336
93	0·367

is described.[910] The electrical conductivity of potassium chloride studied in acetone–water mixtures at 20° and 25°C., over a range 5–100% by volume of water, shows that the conductivity at infinite dilution decreases as the acetone content increases until the mixture contains 85% of acetone. Further increase in the proportion of acetone causes a slight rise in equivalent conductivity at infinite dilution. No minimum is observed at other concentrations.[917] Ion exchange equilibria in a sulphonic acid resin have been studied using potassium chloride in aqueous acetone.[918] Freezing point data for potassium chloride in dioxan–water solutions are in accord with theory.[919] Data on the systems: KCl-*n*-$C_3H_7.O.C_2H_4OH-H_2O$ and KCl-*iso*-$C_3H_7.O.C_2H_4OH-H_2O$, which have two critical solution points, are reported.[910] Potassium chloride is sparingly soluble in diacetone alcohol and very sparingly soluble in methyl *iso*butyl ketone.[920] The systems $KCl-Et_3N-H_2O$ at 0°, 10°, and 15°C.; $KCl-C_5H_5N-H_2O$ at 0°, 20°, 50°, and 80°C.; and $KCl-C_5H_{11}N-H_2O$ at 20°, 40°, 60°, and 80°C., are reported.[921] The electrical conductivities of potassium chloride in pyridine–water mixture (ϵ from 12 to 68), show the salt to be completely ionised in this medium.[922] The solubility of potassium chloride in acetonitrile, at both 18° and 25°C., is $2{\cdot}4 \times 10^{-3}$ g./100 g. solvent.[887] The electrical conductivities at 3°, 20°, and 40°C.[923] and the activity coefficients[924] of potassium chloride in formamide solution (ϵ ranging from 118 to 103, within the temperature range 3° to 40°C.) give no indication of ion association. The densities, viscosities, and conductivities, at 30° to 60°C., of potassium chloride in N-methylacetamide (ϵ = 178·9 at 30°C., 138·6 at 60°C.) for concentrations from 5×10^{-4} to 1 M., show good agreement with theoretical values up to 0·3 M.[925]

Vapour Phase.

The saturation current in potassium chloride vapour at 550°C. between copper electrodes at 90 V. is about 10^{-4} amp., the potassium chloride being dissociated at about 0·002% at this temperature.[926] The heat of dissociation of gaseous potassium chloride is calculated as 101·2 kg.-cal.[927] The vapour of potassium chloride at a pressure of 2 mm. of mercury has an estimated ionisation potential of 5 V.[928] The effect of potassium chloride and potassium chloride–sodium chloride mixtures in a carbon arc is to produce a drop in the potential of the arc.[929] The ionisation produced by potassium chloride in a coal gas flame has been measured.[930] The change in electrical conductivity of hydrogen–oxygen and hydrogen–chlorine flames caused by the addition of potassium chloride, increases initially with the salt concentration, and then passes through a maximum.[931]

Chemical Reactions

Much information concerning the chemical behaviour of potassium chloride in various systems has already been given. *(vide supra.)*

The equilibrium constants for the heterogeneous system: $KCl + HBr \rightleftharpoons KBr + HCl$, are 8·33 and 6·10, at 765° and 850°C., respectively, the heat of reaction being −8500 g.-cal. The solid phase is an ideal solution of the two salts.[932] The reaction between potassium chloride and cæsium bromide,[933] and lithium fluoride, lithium bromide, rubidium fluoride, and cæsium fluoride[934] in the melt is in accord with the law of mass action. In general, the heavier cation and the heavier anion tend to crystallise together. Potassium chloride and caesium bromide react in the dry state, equilibrium being attained in three days at 477°C.[934] In the reaction between potassium chloride and ammonium sulphate, the most complete transformation to potassium sulphate takes place at 700°C. with an excess of not less than 40% of ammonium sulphate.[935] Data on the limits of composition between which reaction takes place in the $(NH_4)_2Cr_2O_7$–KCl and $(NH_4)_2Cr_2O_7$–K_2SO_4–KCl systems, show that for the former, no reaction occurs with more than 13% of potassium chloride. Ternary diagrams showing the limits are reported.[936] The reaction between ammonium bicarbonate and potassium chloride gives a maximum yield of potassium carbonate at 5°C. in 85% ethyl alcohol solution. No potassium carbonate can be produced from aqueous solution.[937]

Selenium oxyfluoride combines with potassium chloride to yield a coloured compound of unspecified composition.[938] Phosphorus pentachloride, which does not normally react with potassium chloride, does so in the presence of iodine monochloride, the compound of the formula $KPCl_6$ being formed in solution.[939, 940] Iodine monochloride may also be used as a solvent in effecting combination with antimony pentachloride to yield the compound $KSbCl_6$.[940] The mixture, after being heated for several hours at 50°–60°C., is extracted with carbon tetrachloride to remove the reaction product. The compounds K_2VCl_6, which is orange-red in colour, and K_2SnCl_6 (in an impure form), may be prepared in a similar manner, using vanadium tetrachloride and stannic chloride respectively.[940] There is some evidence that the vanadium salt is also formed when the products of chlorination of vanadium are passed over potassium chloride. The product is decomposed on heating in a stream of chlorine, the vanadium volatilising apparently as the tetrachloride.[941] The solubility of platinum in aqueous hydrochloric acid, normally minute, is said to be increased so considerably by the presence of potassium chloride as to introduce serious errors into analyses involving the use of platinum vessels. The metal is also attacked by the molten salt in the presence of hydrogen chloride, the compound K_2PtCl_4 being first formed and thereafter decomposing on solidification to yield the salt K_2PtCl_6 and metallic platinum.[942] The action of molten potassium chloride on nickel, copper, and various steels, has also been investigated.[943] Decomposition of the salt begins at 470°, 475°, 480°, 490°, 500°, 505°, and 510°C., on copper, on vanadium, on molybdenum and iron, on tungsten, on manganese, on cobalt, and on zinc, respectively.[944] Gaseous potassium chloride attacks silica to form the compound K_2SiCl_6, but only if hydrogen chloride is present.[945] At 1000°C., silica refractories are but slightly attacked by the dry vapour even after 367 hr., but aluminous materials, and especially fireclay, are less resistant.[946,947] The existence of the compound $KHCl_2$, which is stable only at high temperatures, has been reported.[945] Potassium chloride reacts with boric acid in accordance with the equation: $3KCl + H_3BO_3 \rightarrow K_3BO_3 + 3HCl$. The reaction, which begins at 450°C., is complete at 900°C.[948] The chemical kinetics and mechanism of the decomposition of solid potassium chloride in a stream of nitric acid vapour, air, and water vapour have been investigated with particular reference to the grain size of the salt and the catalytic influence of the water vapour present. The reaction, as represented by the basic equation: $3KCl + 4HNO_3 \rightarrow 3KNO_3 + NOCl + Cl_2 + H_2O$, decreases rapidly in velocity and ceases after only a fraction of the chloride has been converted.[949] Two further investigations of the reaction have been described.[950,951] The formation of microcrystals of potassium nitrate on crystals of potassium chloride, when the latter are exposed to α-rays from polonium in the presence of moist air, has been described. The action is attributed to the oxidation of atmospheric nitrogen to nitrogen peroxide, the latter forming nitric acid with traces of moisture.[952] The conversion of solid potassium chloride to the sulphate by treatment with a stream of sulphur dioxide carrying air and water vapour, and using ferric oxide as a catalyst, has been investigated.[953] The thermodynamics of the reaction of potassium chloride with calcium sulphate have been investigated, particular attention having been paid to the various forms of calcium sulphate which can be employed and to the solubilities of intermediate double salts.[954] The reaction: $2KCl + Br_2 \rightarrow 2KBr + Cl_2$, has been studied at 804° and 905°C., at which temperatures the double anions Cl_2^{2-} and Br_2^{2-} are thought to be present. At higher temperatures, for example 1250°C., the latter are said to split into ions carrying single charges.[955] With bromine and iodine, potassium chloride in aqueous solution forms, respectively, the complex trihalides $KClBr_2$[956] and $KClI_2$,[956,957] the equilibrium constants of which are $1{\cdot}8 \times 10^{-1}$ and $3{\cdot}0 \times 10^{-1}$ at 16°C. The solubilities of iodine and bromine in solutions of potassium chloride of up to several moles/litre, determined at 30°C., have provided evidence for polyhalide formation.[958] Crystals of potassium chloride, after being heated in vacuo, show an alkaline reaction to phenolphthalein in aqueous solution, the effect being greater if the crystals are crushed before heating, presumably because it is due to hydrolysis by adsorbed water.[959] The degree of ionisation of potassium chloride directed as a molecular beam against a pure or an oxidised tungsten surface has been calculated as a function of temperature from the value of the positive ion current. On oxygen-free surfaces at 1800°–2380°K., surface dissociation of the halide molecule is followed by the liberation of chlorine and partial ionisation of the potassium.[960]

Potassium chloride has been used both as a catalyst and as a promoter of other catalysts. A pyrites ash promoted with 1% potassium chloride is used in the conversion of hydrogen–carbon monoxide mixtures to hydrocarbons. The proportion of olefins in the product, as well as the overall yield, is increased by promotion of the catalyst.[961] Ethyl chloride is converted to ethylene and hydrogen chloride by passage over heated potassium chloride or other catalysts promoted with potassium chloride.[962] The addition of potassium chloride to potassium chlorate accelerates the thermal decomposition of the latter;[963] similarly for potassium perchlorate the rate of thermal decomposition is accelerated, but in this case the induction period is reduced.[964] In both cases the catalytic activity varies with the history of the potassium chloride employed. Potassium chloride appears to act catalytically in the oxidation of carbon by air by reason of the ability of the chloride ion to act as an oxygen carrier by the formation of perchlorate.[965] The ignition temperature of carbon is thereby lowered by about 100°C.[966] The reaction of nitric oxide and carbon at elevated temperatures is catalysed by potassium chloride.[967] Potassium chloride exerts an inhibiting effect on the explosion of "nitrogel" and ammonium nitrate mixtures.[968]

The solution of dolomite in sulphuric acid[969] and of aluminium in hydrochloric acid[970] is accelerated by the addition of potassium chloride. Potassium chloride along with many other salts catalyses the decomposition of hydrogen peroxide, the catalytic activity of the salts following closely the Hofmeister series for the adsorption of ions from solution.[971] The exchange of sulphur in the sulphur dioxide–thionyl bromide system is catalysed by potassium chloride.[972] The retardation of the iodine–ferrocyanide reaction[973] and the persulphate–oxalate reaction[974] by the addition of potassium chloride is reported.

The recombination of hydrogen and oxygen atoms and hydroxyl radicals is particularly efficient on a surface coated with potassium chloride.[975] This ease of recombination has a direct effect on the explosion limits of the hydrogen–oxygen mixture,[976] and on the formation of hydrogen peroxide in this combustion reaction.[977] In the case of lead and potassium chloride the activity of the catalyst is merely an additive function of the separate lead and potassium chloride activities.[978] Potassium chloride-coated surfaces have been employed in numerous other investigations of chain reactions, such as the oxidation of *cyclo*propane,[979] formaldehyde,[980] and hydrazine,[981] or the thermal decomposition of normal paraffin hydrocarbons.[982] Potassium chloride dust has been shown to be an effective quenching agent for an ignited mixture of methane and air.[983]

Quantitative observations of the corrosive action of aqueous potassium chloride on various common metals[984] have given much information about the structure, composition, and mode of formation of the resulting corrosion products, and in many of the sources cited below the mechanism of the particular corrosion process is discussed on theoretical grounds. A general survey of the phenomenon covering both ferrous and non-ferrous metals, in the presence and absence of air, has been published.[985] The rate of attack on magnesium immersed in a 2·0 N. solution of the salt at 10–50°C. is determined firstly by the chemical reaction and secondly by the diffusion of reaction products.[986] From studies of the kinetics of the corrosion of magnesium in potassium chloride it is postulated that bound water reacts more rapidly with magnesium than does free water.[987] If in addition to potassium chloride the solution contains the chloride of a metal more noble than magnesium, local cells are formed, and under given conditions corrosion proceeds at a constant speed.[988] The activation energy of the reaction increases with increasing concentration of the second chloride.[989] The structure, distribution, and composition of deposits resulting from the immersion of aluminium in 0·001–2·0 N. solutions of potassium chloride have been described and their mode of formation has been explained.[990] At 20°C., over a period of 50 days, the rate of corrosion over the range 0·001–3·0 N. may be expressed by the equation: $\Delta g = kC^a$, where Δg represents the loss in weight and C the concentration, k and a being constants. For shorter periods of, say, 15 days the equation is, however, invalid.[991] The corrosive action of 23–25% solutions of potassium chloride on age-hardened duralumin, on copper–aluminium alloy No. 12, on silium, and on annealed and hard rolled sheet aluminium has also been studied. A film of hydrogen bubbles and a white deposit appear almost immediately at room temperature and pronounced etching follows with the two alloys first mentioned.[992] The rate of corrosion of lead in 0·001–2·0 N-potassium chloride at 20°C. first increases with concentration, attaining a maximum at 0·05 N., and thereafter decreases until at 2·0 N. a second increase begins. The primary and secondary corrosion products are, respectively, lead chloride and a basic salt, thought to have the composition $PbCl_2,2Pb(OH)_2$.[993] In aerated solutions of potassium chloride at dilutions exceeding 0·001 N., the compound $2PbCO_3,Pb(OH)_2$ is formed, while in those in the range 0·001–0·5 N., the basic chloride mentioned above again appears. The increased rates of corrosion at 0·005 N. and above 2·0 N. have been attributed, respectively, to the crystalline structure of the deposit and to the formation of water-soluble lead chloride complexes.[994] Investigation of the corrosive action of a boiling 1·0 N. solution of the salt on copper, on lead, and on zinc, in the presence of air shows that copper is attacked a little, lead more so, and zinc scarcely at all, under these conditions. The addition of sodium acetate, boric acid or acid sodium phosphates does not affect the process to any marked extent, indicating that hydrogen ion concentration plays no part in the reaction.[995] Solutions containing 300–350 g./l. of potassium chloride in addition to 80–100 g./l. of sodium chloride, 50–70 g./l. of potassium chlorate, and 0–3 g./l. of sodium hydroxide are without corrosive action on lead and iron up to periods of 3 days. In the absence of sodium hydroxide, however, the metals corrode to an extent exceeding 300 g./sq. m. in that period.[996] The corrosion of steel immersed at 20°C. in 0·001–2·0 N. solutions of potassium chloride for several weeks decreases as the concentration increases within this range. The rate of attack slackens with time, becoming constant after 2 days.[997] It has been stated that corrosion by a 0·1 N. solution of the salt slightly exceeds that of a 1·0 N. solution,[998] but another author says that under static conditions, the rate over a 15 day period is independent of concentration in the range 0·001–1·0 N.[999] In a 1 N. solution, an increase in carbon content of the steel causes a moderate acceleration of the rate of corrosion.[999] The existence of radial currents during the corrosion in air and in nitrogen of a pole-piece of a mild steel electromagnet by a drop of potassium chloride solution adhering to it, has been demonstrated by showing that the drop is deflected rotationally on reversal of the field current of the magnet. The rotation in nitrogen is less than in air, its direction depending on that of the field flux.[1000] The corrosion of steel by nitric acid is inhibited by potassium chloride owing to cathodic processes.[1001] At 35°C., and for relative humidities exceeding 50%, solid potassium chloride is sufficiently deliquescent to corrode mild steel. Protection by heavy greasing has been proposed.[1002] The corrosion of nickel, copper, Ni–Cu alloys, Ni–Fe–Cr alloys, bronze, brasses, aluminium and its alloys and iron and steel specimens in contact with the solid salt under the influence of atmospheric conditions of temperature and humidity has been investigated.[1003] The rate of corrosion of mild steel by dilute solutions of potassium chloride is expressed by the equation: $i_0 = Ip Iq/(Ip + Iq)$, i_0, Ip, and Iq representing the corrosion current, the cathodic protection current, and the anodic protection current, respectively. Values obtained from this relation accord to within 10% of those observed experimentally.[1004] In a corrosion cell consisting of iron electrodes immersed in neutral solutions of potassium chloride differing in temperature, the metal in the cooler section constitutes the cathode, and in the warmer solution the anode. The addition of potassium nitrate causes a reversal in polarity and the formation of thin films on the surface of the iron. When the combined normality of the solution exceeds about 0·1, the current generated is sufficient to provide almost complete protection of the cathode from the effects of local corrosion.[1005] Potassium chloride inhibits to some extent the corrosion of certain nitrided steels by dilute sulphuric acid, but it does not suppress localized corrosion.[1006] The exposure of zinc plating to air increases its resistance to corrosion by aqueous potassium chloride.[1007] In fully oxygenated solutions of the salt, the corrosion rate for zinc is greatest at concentrations between 0·001 and 0·1N. At greater dilutions, the rate is controlled by the chloride ion and at higher concentrations by the oxygen. In open vessels, the rate decreases rapidly with depth of immersion of the specimen, up to a depth of 1·5 cm. The onset and development of the corrosion process have been described and explained.[1008] As the concentration of the solution increases corrosion of the zinc increases to a maximum velocity, and decreases as the solution approaches saturation. When the concentration exceeds 0·0001N., hydrogen is evolved. In later stages, the corrosion rate depends both on concentration and on the rate of withdrawal of chloride ion either by precipitation or by other processes.[1009] The kinetics of the onset of the corrosion of copper by aqueous potassium chloride are of the first order with respect to the concentration of oxygen and of hydrogen ion.[1010] The corrosion of nickel, copper and various alloy steels by fused potassium chloride and by the vapour has been investigated.[1011]

Analytical

The separation of potassium chloride from lithium and sodium chlorides is effected by paper chromatography, using as solvent absolute methyl alcohol or 80% ethyl alcohol–20% water mixture (by volume), or 80% acetone–20% water (by volume).[1012] The method may be applied quantitatively.[1013] A method for the continuous separation of potassium chloride and lithium chloride by paper chromatography is described.[1014]

A mixture of ethyl alcohol and ether has been employed to separate quantitatively magnesium chloride and potassium chloride, the former being readily soluble.[1015]

When crystals of potassium chloride are dried at 500°C., water is lost and a weight loss of 0·06–0·97% occurs. At 900°C., there is a further loss of 0·07–0·11%, to give completely anhydrous material.[1016]

Ion exchange techniques are readily adapted to the analysis of potassium chloride solutions.[1017]

For the analysis of mixtures of sodium and potassium chlorides, electrolysis at a controlled potential can be applied, although the results are not particularly good for potassium.[1018]

Flame photometry has been applied successfully to the determination of potassium chloride in barium chloride.[1019] Further application of flame photometry can be expected, employing more sensitive flame spectrophotometers. The separation of potassium, rubidium, and cæsium chlorides by extraction with a solvent containing hydrochloric acid and aqueous alcohol (4ml. water and 10ml. HCl-saturated ethyl alcohol) is reported; the solubilities in 10 ml. of this solvent being 0·075, 1·22, and 11·4 mg., respectively.[1020] Various potentiometric methods have been suggested, among which can be mentioned the high frequency titration of potassium chloride by silver nitrate or mercuric nitrate in the concentration range 0·1–0·01N.,[1021] and the direct potentiometric titration, using a glass electrode, of 0·1N-potassium chloride with 0·1N-silver nitrate.[1022]

Applications

In addition to the well-known uses of potassium chloride as a fertiliser and as a heavy chemical for the industrial production of a large number of potassium compounds, the salt has numerous other applications. It is employed extensively as a constituent of fluxes,[1023-1025] and of salt baths[1026] in metallurgical operations, and of agents for degassing[1027] and purifying various non-ferrous alloys.[1028] A mixture of the chlorides of potassium and lithium at 450°C. extracts, almost quantitatively, rare-earth metals formed as fission products in uranium–bismuth fuels.[1029] Explosions in petroleum pipe-lines may be arrested by the action of a dust screen of the salt set up by the incident pressure wave,[1030] and the employment of porous flame traps coated with the salt has been suggested to control the combustion zone in a device, using a gas turbine, which may be used for the production of acetylene.[1031] Potassium chloride crystals containing silver may be used in scintillation counters:[1032] reference to other systems suitable for the detection of radiation have already been made (see page 1672). The molten compound $KCl,SnCl_2$ has been suggested as a tinning dip for various ferrous and copper alloys.[1033] Potassium chloride may be used as a constituent of long-persistence screens in cathode ray tubes[1034] and of ultra-violet fluorescent materials.[1035] A eutectic mixture of the salt with lithium chloride has a higher rate of change of resistance with temperature in the solid than in the molten state, and so may be used for the thermoelectric control of various electrical devices.[1036] The use of a battery consisting of an assembly of ion-exchange membranes, with solutions of potassium chloride in the various compartments, has been suggested as a source of electrical energy.[1037]

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SECTION LII

POTASSIUM BROMIDE

By W. H. LEE and M. F. C. LADD

Preparation

The preparation of chemically pure potassium bromide from pure starting materials, rather than the attempted purification of a less pure salt, is recommended. In the Balard process, potassium hydroxide is treated with bromine; the reduction of the bromate, formed simultaneously, is best effected by hydrogen sulphide, or by barium hydrogen sulphide, $Ba(HS)_2$. Potassium bromide has also been manufactured by treating bromine, under water, with crude barium sulphide, BaS: the hydrogen bromide and barium bromide thus formed are allowed to react with solid potassium carbonate.[1]

Commercial grade potassium bromide may be made by treating iron scrap with steam and bromine vapour forming Fe_3Br_8, and adding potassium hydroxide solution: Fe_3O_4 is precipitated, and the potassium bromide is then recrystallised.[2]

Substantially pure potassium bromide is obtained by treating potassium carbonate with free bromine, followed by fractional crystallisation of the product.[3] The formation of bromate, on heating, is prevented by the presence of activated carbon;[4] alternatively, this reaction may be carried out in the presence of ammonia.[5]

From technical grade potassium chloride, pure potassium bromide was obtained, in 86% yield, by distillation with 48% hydrobromic acid (the constant-boiling mixture). All the hydrogen chloride, with a very small amount of hydrogen bromide, was removed, and the salt separated in the flask.[6]

A review of the various commercial methods for the preparation of potassium bromide has been published.[7]

Potassium bromide may be purified as follows. Sulphate is removed by treatment with a barium halide; hydrogen peroxide is added to oxidise iron, and alkaline earths present are precipitated as carbonates; on boiling the alkaline solution, aluminium, magnesium, and silicon are removed, and after acidification and removal of carbon dioxide, crystallisation yields the purified salt.[8]

Large crystals of potassium bromide have been obtained by drawing a water-cooled spindle up from the melt; such crystals are suitable for infra-red dispersion measurements.[9] Another technique for producing large single crystals of potassium bromide, suitable for optical use, involves lowering a crucible charged with the bromides and having a pointed base through a temperature gradient which includes the melting point of the salt.[10]

Special furnaces for growing single crystals of several pounds weight are described; the crystal is obtained by progressively racking up a seed suspended above the melt.[11] Large single crystals have also been grown by floating a crystal on the surface of the molten potassium bromide, and the elimination of cooling strain has been discussed.[12]

X-Ray measurements by the powder method indicate that up to 1% of isomorphous impurities has negligible effect upon the unit cube distance a.[13]

The crystalline form may be modified, however, by growing from solutions containing impurities; for example, addition of sodium nitrate (*d* 5·07) to potassium bromide solution produces octahedral faces on the bromide crystals (*d* 4·70), but the effect is not observed with sodium chloride (*d* 3·07), these figures being the interionic distances, in A., in the (111) plane, all the ions in one plane being alternately metal and halogen.[14]

Physical Properties

The lattice constant and the density of potassium bromide have been redetermined, with the results listed in Table I.

TABLE I.- LATTICE CONSTANT AND DENSITY OF POTASSIUM BROMIDE

d	*a*	*t*°	ref.
2·746	—	15	15
2·7533	6·5966	25	16
2·749	6·590	25	Mellor, II, 579

It seems probable that the best values of lattice constant and density are those of ref. 16.

The lattice energy has been re-calculated, and the values obtained are listed in Table II.

TABLE II.- LATTICE ENERGY OF POTASSIUM BROMIDE

U (kg.-cal./mole)	160	161	162	159	160
Ref.	17	19	20	20	Mellor, II, 579
Method	*a*	*b*	*c*	*d*	

a: From thermal ionisation, and estimation of ion-concentration in the vapour (*vide* Mayer[18]).

b: Calculation, assuming basic ionic radii.

c: Modified Born–Haber cycle.

d: Electrostatic model calculation, allowing for dipole-dipole, and dipole-quadrupole, interactions.

Oriented overgrowths are reported for potassium bromide on lithium chloride, potassium chloride, sodium chloride, and Joplin galena – all these being cubic structures. The crystallographic axes were parallel to those of the substrate.[21, 22, 23] On orthoclase, various orientations of potassium bromide were noted.[24] On mica, potassium bromide is oriented to the larger atomic network of the substrate.[25] On calcium carbonate and sodium nitrate, regularity is shown by deposits of potassium bromide up to 10 A. thick, but random orientation is observed at thicknesses over 150 A.[26]

The refractive indices of potassium bromide, at wave-lengths from 7699 to 4047 A., are recorded in Table III.[27]

TABLE III.- THE REFRACTIVE INDEX OF POTASSIUM BROMIDE, FROM 7699 A. TO 4047 A.

λ, A.	Source of radiation	n_{20}	$n_{26\cdot4}$
7699	K	1·54780	1·54980
7065	He	1·55245	1·55217
6678	He	1·55444	1·55416
6563	H	1·55503	1·55475
5893	Na	1·55986	1·55958
5877	He	1·55998	1·55970
5461	Hg	1·56395	1·56367
5016	He	1·56948	1·56920

continued on following page

TABLE III.- CONTINUED.

λ, A.	Source of radiation	n_{20}	$n_{26·4}$
4922	He	1·57085	1·57057
4861	H	1·57181	1·57153
4713	He	1·57429	1·57401
4471	He	1·57896	1·57868
4358	Hg	1·58149	1·58121
4047	Hg	1·58976	1·58948

The temperature coefficient was found to be 4·4 × 10^{-5} per °C.

Measurements of refractive indices have been made over the range 14 μ to 26·7 μ, using a potassium bromide crystal prepared as previously described,[9] having a facial area of 6cm. × 8·5cm. The results are given in Table IV.[28]

TABLE IV.- REFRACTIVE INDEX OF POTASSIUM BROMIDE, FROM 14μ TO 26·7μ

λ, μ	n_{38}	λ, μ	n_{38}
14	1·5141	21	1·4847
15	1·5107	22	1·4793
16	1·5071	23	1·4733
17	1·5030	24	1·4672
18	1·4989	25	1·4606
19	1·4944	26	1·4536
20	1·4896	26·7	1·4481

The dispersion of potassium bromide in the infra-red is also shown in Fig. 1.[29]

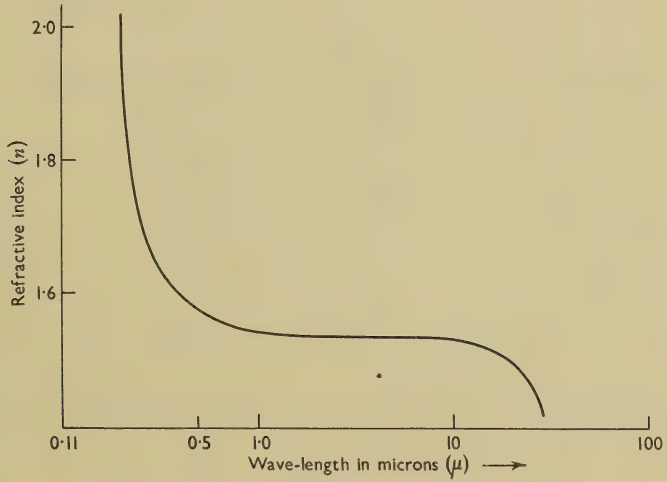


FIG. 1.- DISPERSION OF CRYSTALLINE POTASSIUM BROMIDE IN THE INFRA-RED

The vapour pressure of fused potassium bromide has been measured at temperatures between 1100° and 1375°, as recorded in Table V.[30] In this Table, $t°_{\text{calc.}}$ is the temperature calculated from the relationship:-

$$\log p_{\text{atm.}} = \frac{-38200}{4{\cdot}57\,T} + 5{\cdot}055,\ T \text{ being in } {}^{\circ}\text{K}$$

The melting point of potassium bromide is 728°, and the boiling point 1376°.

TABLE V.- THE VAPOUR PRESSURE OF POTASSIUM BROMIDE

t°C.$_{\text{expt.}}$	p, mm.	t°C.$_{\text{calc.}}$	Δt°
1095	70·8	1098	−3
1110	76·8	1106	+4
1165	128·5	1159	+6
1237	215·7	1238	+2
1241	266·1	1242	−1
1325	526·2	1328	−3
1328	529·1	1332	−4
1375	761·4	1376	−1
1380	756·2	1378	+2

The vapour pressure of potassium bromide at 1250°C. is 280±2mm.[31] The compressibility, κ, of potassium bromide, and its variation with temperature and pressure, have been measured, with the following results:-[32]

$10^{12}\kappa_{+30}$	$10^{12}\kappa_{-273}$	$(\partial\kappa/\partial P)_T$*	$(\partial\kappa/\partial T)_{P,30}$ 75
6·70	5·5	$3{\cdot}18\times10^{-11}$	$6{\cdot}0\times10^{-4}$

* for pressures up to 12,000 atm., and t = 30°–75°C. The estimated errors are:-

$$\kappa,\ <1\%;\ (\partial\kappa/\partial P)_{T},\ 5\%;\ (\partial\kappa/\partial T)_{P},\ 20\%$$

Some elastic properties of potassium bromide have been determined in flexure, and are quoted below. The thermal expansion was also measured in this study of optical materials,[33] and results are listed in Table VI. Other properties are:- Young's modulus, 2·7 × 10^{11} dynes/cm.^{2}; apparent elastic limit, 1·1 × 10^7; modulus of rupture, 3·3 × 10^7; modulus of rigidity (measured in torsion), 0·508 × 10^{11}; elastic moduli: c_{11} 3·45, c_{12} 0·540, c_{44} 0·508 × 10^{11}. The units for all the above properties are dynes/cm.^{2}

TABLE VI.- COEFFICIENT OF EXPANSION OF POTASSIUM BROMIDE, $a\times10^6$/°C.[33]

t° (range)	$a\times10^6$	t°	$a\times10^6$
−50 to +20	41	100	36
20 to 100	42	120	38
20 to 200	41	140	41
		160	42
		180	43
		200	44

Values of the thermal resistivity of potassium bromide, at various temperatures, are listed in Table VII.[34]

The specific heat of potassium bromide, within the range 20° to 660°, is given by the equation:-

$$c_p = 0{\cdot}1021 + 1{\cdot}94\times10^{-5}t$$

Deviations from this expression are generally of the order of 0·1%. The heat capacity is given by:-[35]

$$C_p = 12{\cdot}11 + 4{\cdot}61\times10^{-3}t$$

Precision measurements of the enthalpy of potassium bromide are recorded in Table VIII.[36]

The enthalpy, and free energy, of formation of potassium bromide, have been re-determined, as follows:-[37]

$$\Delta H^{\circ}_{f}\ 25^{\circ},\ = -94{\cdot}2\text{kg.-cal.}\quad \Delta G^{\circ}_{f},\ 25^{\circ},\ = -90{\cdot}5\text{kg.-cal.}$$

These values are in good agreement with the results of electromotive force measurements on amalgam cells:-[37]

$$\Delta H^{\circ}_{298} = -93{\cdot}89\text{kg.-cal.},\ \Delta G^{\circ}_{298} = -90{\cdot}48\text{kg.-cal.}$$

The entropy of potassium bromide is 23·05g.-cal./mole°C., at 298·16° K.[38]

TABLE VII.- THERMAL RESISTIVITY OF POTASSIUM BROMIDE

T°K.	ρ	T°K.	ρ
89·5	7·74	14·98	1·44
87·5	7·52	4·65	0·81
80·3	7·15	4·18	0·83
78·2	7·06	3·89	0·86
20·0	2·05	3·46	0·95
18·9	1·95	3·13	1·09
18·0	1·89	2·93	1·17
16·8	1·77	2·63	1·26
15·92	1·63	2·21	1·59
15·28	1·51	2·04	1·80

ρ, thermal resistivity, in watts/cm.°C.

TABLE VIII.- ENTHALPY AND HEAT CAPACITY, OF POTASSIUM BROMIDE

t°	H, kg.-cal./mole	C_p, g.-cal./mole
300	3·85	13·40
350	4·53	13·65
400	5·22	13·90
450	5·92	14·10
500	6·63	14·29
550	7·35	14·47
600	8·08	14·64
650	8·81	14·81
700	9·56	14·97
730	10·01	15·06

The thermal expansion of potassium bromide at low temperatures has been determined by toluene pycknometers and gas-displacement pycknometers, which are described.[39]
Within the range −184° to −79°, the volume expansion coefficient, 3α, is 0·000101; within the range −79° to 0°, 3α = 0·000110. Within the range 0° to 50°, 3α = 0·000118.[40]

Thermal expansion coefficients have also been determined by X-ray measurements, and the values compared with those determined by macroscopic methods.[41]

Temperature range	18 – 100°	18 – 190°
X-Ray value, α	$40{\cdot}5 \times 10^{-6}$	$41{\cdot}7 \times 10^{-6}$
Macroscopic value, α	$40{\cdot}8 \times 10^{-6}$	$41{\cdot}4 \times 10^{-6}$

The rate of vaporisation of potassium bromide depends upon particle size, and is a minimum at 4μ;[42] the heat of vaporisation is 40·8kg.-cal./mole.[43] The boiling-point, and the critical temperature, are 1388°C, and 2575°C, respectively.[43]

The electrical conductivity of single crystals, and of polycrystalline aggregates, of potassium bromide, over the temperature range 490° to 730°, has been determined, and the results are recorded in Table IX.[44]

TABLE IX.- THE ELECTRICAL CONDUCTIVITY OF SINGLE CRYSTALS, AND OF POLYCRYSTALLINE AGGREGATES OF POTASSIUM BROMIDE

t°	$10^6\kappa$, single crystals	$10^6\kappa$, polycryst. aggregates
730	120	120
710	72·5	72·5
690	44·6	44·6
670	25·7	27·6
650	15·5	17·4
630	9·13	10·5
610	5·50	6·61
590	3·22	4·20
570	1·95	2·63
550	1·20	1·74
530	0·725	1·18
510	0·458	0·830
490	0·282	0·603

The average deviation of these results is ±14%. The melting point of potassium bromide quoted by the authors is 740° (but see page 1741). The electrical conductivity has aslo been determined for mixed crystals of potassium bromide and potassium chloride, of composition 5·3 wt.-% KBr; these results are given in Table X.[44]

TABLE X.- THE ELECTRICAL CONDUCTIVITY OF SINGLE CRYSTALS, AND OF POLYCRYSTALLINE AGGREGATES, OF KBr/KCl MIXED CRYSTALS, OF COMPOSITION 5·3 wt.-% KBr

t°	$10^6\kappa$, single crystals	$10^6\kappa$, polycryst. aggregates
740	–	159
720	85·0	85·0
700	41·7	48·0
680	23·5	28·9
660	13·8	18·0
640	8·30	11·5
620	4·79	7·78
600	2·82	4·92
580	1·70	3·17
560	1·00	1·95
540	0·618	1·25
520	0·400	0·741

The average deviation of these results is ±12·5%. The melting point of the mixed crystal was 776°.

The electrical conductivity of molten potassium bromide, at the melting points of tin, lead, and zinc, has been determined.[45]

t°	232(m.p.Sn)	327(m.p.Pb)	419(m.p.Zn)
$10^8\kappa$	0·201	8·43	279 mhos.

These results may be expressed to within 0·5% by the relationship:-[46]

$$\log \kappa_t = a + bt$$

The molar conductivity of potassium bromide has been determined up to 1600°; over the temperature range 745·2° to 868·6° it follows the relationship:-[47]

$$\Lambda_t = 90{\cdot}09 + 0{\cdot}1906\,(t - 750^\circ)$$

From the measurement of electrical conductivities, the terms A_κ and E_κ, in the equation:-

$$\kappa = A_\kappa \cdot \exp.(E_\kappa/RT)$$

have been determined, for the molten salt mixtures potassium bromide–barium bromide, potassium bromide–potassium nitrate, and potassium bromide–sodium chloride. These terms, together with the constants a and b in the density equation:-

$$\rho_{t^\circ} = a + bt^\circ$$

are recorded in Table XI.[48]

TABLE XI.- CONSTANTS OF THE CONDUCTIVITY, AND DENSITY, EQUATIONS, FOR SOME MOLTEN SALT MIXTURES, AT 800°C.

System	KBr, (mol.-%)	A_κ	E_κ (kg.-cal./mole)	a	$10^4 b$
$KBr/BaBr_2$	100	5·99	2·64	2·725	7·94
	79·5	8·10	3·74	3·318	9·37
	75·7	8·61	3·92	3·324	8·49
	66·7	9·06	4·20	3·558	8·96
	60·0	10·13	4·78	3·720	9·30
	48·0	12·5	5·12	3·932	9·06
	35·0	15·9	5·75	4·117	8·75
	25·0	16·3	5·84	4·425	10·23
	15·0	23·4	6·75	4·353	7·25
	0			4·783	9·24
KBr/KNO_3	100	7·63	3·11	2·725	7·94
	85·0	6·47	2·78	2·635	8·01
	66·7	6·47	2·78	2·476	7·30
	50·0	7·56	3·05	2·415	7·79
	33·3	7·07	2·93	2·285	7·27
	15·0	7·59	3·01	2·186	7·14
	0	8·55	3·15	2·116	7·29
KBr/NaCl	50·0	3·08	10·0	2·447	7·23

The specific conductivity of the system potassium bromide–potassium chloride has been studied, at temperatures above the melting point.[49] In Fig. 2 the specific conductivity κ is plotted as a function of % composition, for $t = 645^\circ$; in Fig. 3, κ is plotted against $1/T^\circ$, for the 85 mol % KBr mixture. The melting point-composition curve is plotted in Fig. 4,[50] and compared with the results of this conductivity investigation.

The decomposition potential of fused potassium bromide has been determined, over the temperature range 736° to 962°;[51] the results are listed in Table XII.

A more recent investigation gives agreement at 782° (E = 3·00 volts), but differs at 842° (E = 2·38 volts).[52]

The order of the decomposition potentials of metals in molten salt mixures differs with temperature and with composition of melt; in a potassium bromide–sodium bromide melt, the order was Na, Mn, Be, Al, Tl, Zn.[53]

The dielectric constant of potassium bromide has been measured at a number of frequencies, between 250 and 3×10^7 cycles per second. No definite dependence of dielectric constant upon frequency was found: the dielectric constant of potassium bromide determined by a resonance method is 4·61.[54]

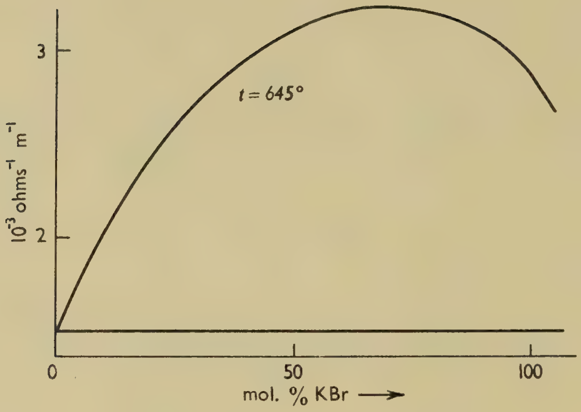


FIG. 2. SPECIFIC CONDUCTIVITY OF KCl-KBr SOLID SOLUTION

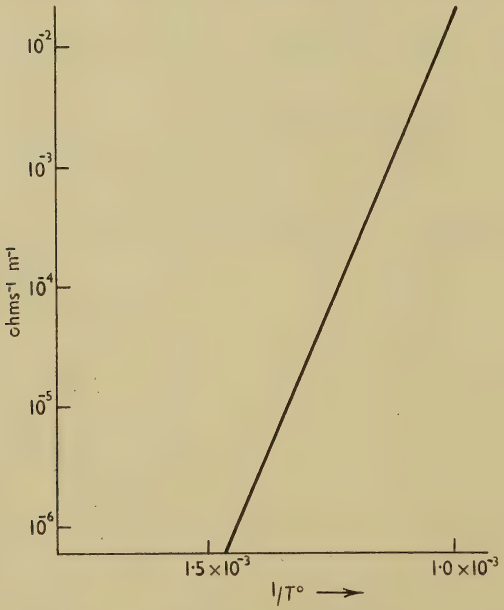


FIG. 3. SPECIFIC CONDUCTIVITY OF 85 MOL % KBr – 15 MOL % KCl SOLID SOLUTION

The Stark method gives the value 4·87.[55] The variation of dielectric constant with pressure has been determined:-[56]

$$-d\ \ln.K/dp = (1·17 \pm 0·09) \times 10^{-5}$$

The dielectric strength of potassium bromide is $0·7 \times 10^6$ volts/cm.[57,58] Mixed crystals of potassium bromide and potassium chloride show additivity of lattice constant *a*, and the substitution in the lattice is random.[59,60,61] Equilibrium is reached by growing the crystals from solution, or from the melt.[62] Thus the heat of solution is the same for mixed crystals derived from the melt or grown from solution. These heats of solution are listed in Table XIII.[63] The heat of solution of potassium bromide, at $t°$, is found to be represented by:-

$$H_s = -43{\cdot}69 + 0{\cdot}309(t - 15)$$

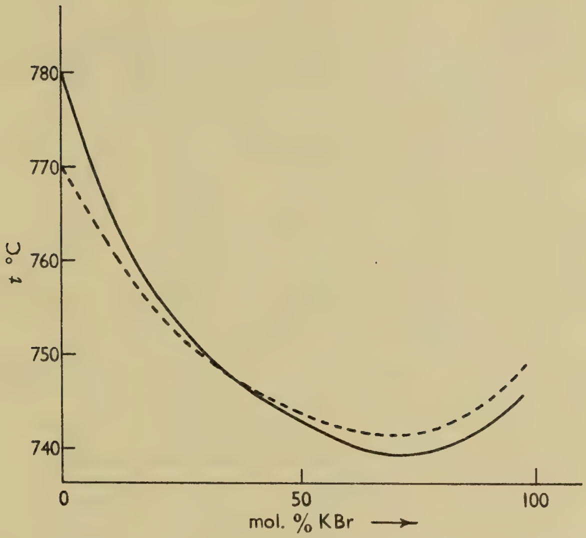


FIG. 4. MELTING POINTS OF KCl-KBr SOLID SOLUTIONS
Solid line — ref. 50
Dashed line --- ref. 49;
temperature at which specific conductivity = $3{\cdot}2 \times 10^3$ ohm^{-1} m^{-1} raised 100°

TABLE XII.- DECOMPOSITION POTENTIAL OF FUSED POTASSIUM BROMIDE, AT VARIOUS TEMPERATURES

$t°$	E volts	$t°$	E volts	$t°$	E volts
736	3·084	775	3·024	881	2·878
736	3·074	795	3·002	899	2·850
739	3·065	812	2·968	917	2·824
740	3·070	838	2·940	935	2·810
745	3·072	860	2·886	962	2·764
760	3·038	870	2·876		
768	3·022	875	2·886		

TABLE XIII.- HEATS OF SOLUTION OF POTASSIUM BROMIDE–POTASSIUM CHLORIDE MIXED CRYSTALS, AT 14·5°C.

Wt.-% KBr	Heat of Solution, g.-cal./g.	
	from soln.	from melt
0	−60·8	−60·9
35·1	−53·2	−52·3
61·5	−47·6	−47·2
81·2	−45·0	−44·3
100	−43·2	−43·1

The specific gravity and specific volume of potassium bromide–potassium chloride mixed crystals, have been determined, and are recorded in Table XIV.[63]

The system potassium bromide–potassium iodide shows additivity over a limited range only, and a minimum lattice constant is obtained.[64] The system potassium bromide–ammonium bromide forms true mixed crystals of the sodium chloride type, up to 40% NH_4Br, and the law of additivity holds over this range.[65]

Lattice constants have been determined, for the system potassium bromide-rubidium bromide; they are given in Table XV.[66]

TABLE XIV.- SPECIFIC GRAVITY AND SPECIFIC VOLUME OF POTASSIUM BROMIDE–POTASSIUM CHLORIDE MIXED CRYSTALS, FROM THE MELT, TEMPERATURE RANGE 16°–18°C.

Wt.-% KBr	S.G.	Calc. Sp. Vol.
0	1·994	–
27·3	2·123	0·4575
43·3	2·236	0·4313
61·5	2·386	0·4023
75·6	2·518	0·3798
90·4	2·649	0·3556
100·0	2·744	–

TABLE XV.- LATTICE CONSTANTS OF MIXED CRYSTALS OF POTASSIUM BROMIDE–RUBIDIUM BROMIDE, AT 25°C.

Mol.-% KBr	*a*, A.	Mol.-% KBr	*a*, A.
0	6·894	34·2	6·793
2·0	6·888	49·2	6·746
4·7	6·890	73·2	6·677
9·2	6·859	90·0	6·628
20·3	6·834	100·0	6·598

The heat of formation of mixed crystals of potassium bromide (40%) and potassium chloride (60%) is approximately 230kg.-cal./mol., and varies with annealing time.[67]

The molar heat capacities of solid solutions of potassium bromide-potassium chloride are recorded as functions of temperature in Table XVI.[68]

TABLE XVI.- MOLAR HEAT CAPACITY DATA FOR POTASSIUM BROMIDE–POTASSIUM CHLORIDE MIXED CRYSTALS, CONSTANTS IN THE EQUATION:- $C_p = a + 10^3\beta t - 10^6\gamma t^2 \pm 0{\cdot}06$ g.-cal./mol.°C.

Mol.-% KBr	a	β	γ
0	10·55	6·90	3·52
25	10·74	6·40	3·25
50	11·21	4·45	1·22
75	11·33	4·23	1·19
100	11·51	3·55	0·50

The surface tensions of molten salt mixtures have been determined, and are shown as functions of composition in Figs. 5, 6, and 7.[69]

The electrical conductivity, and viscosity, of molten potassium bromide-silver bromide mixtures have been studied, at temperatures between 350° and 600°,[70] as given in Table XVII.

The magnetic properties of solid solutions have been studied.[71] For the systems potassium bromide–sodium bromide and potassium bromide–potassium chloride the molar susceptibilities are listed in Tables XVIII and XIX.

In the mixed crystal series potassium bromide–potassium iodide, a minimum in dielectric strength and a maximum in dielectric loss occur at 50% KBr, although for individual alkali halides the dielectric loss decreases, and the dielectric strength increases, with increasing lattice energy.[72]

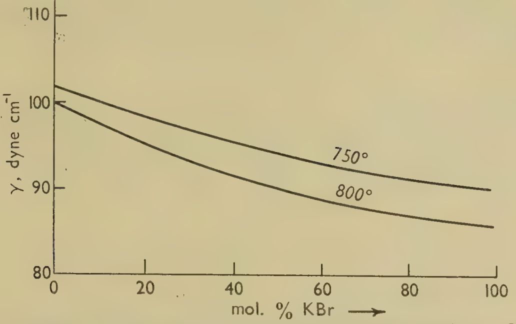


FIG. 5. RELATIONSHIP BETWEEN SURFACE TENSION AND COMPOSITION FOR THE SYSTEM KBr-KCl AT 750° AND 800°C

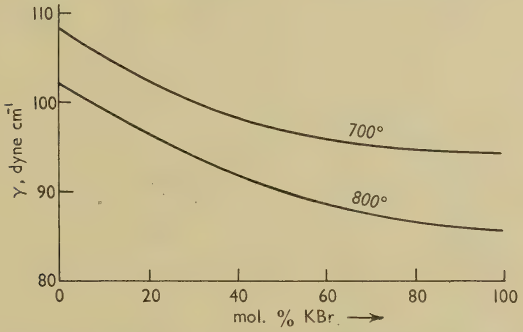


FIG. 6. RELATIONSHIP BETWEEN SURFACE TENSION AND COMPOSITION FOR THE SYSTEM KBr-NaBr AT 700° AND 800°C

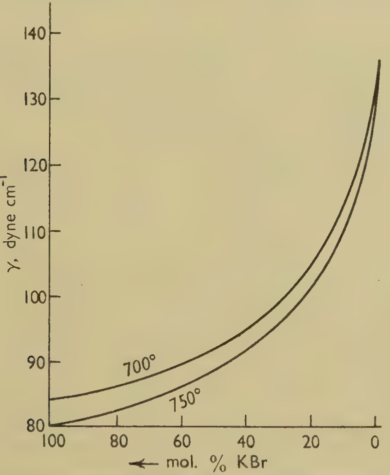


FIG. 7. RELATIONSHIP BETWEEN SURFACE TENSION AND COMPOSITION FOR THE SYSTEM KBr-AgBr AT 700° AND 750°C

X-Ray powder photographs have been used to study the rate of formation of solid solutions of the components potassium bromide–potassium chloride at several temperatures. It was found that the rate of dissolution of potassium chloride in potassium bromide was greater than that of potassium bromide in potassium chloride. Equilibrium was very rapidly attained at 700°, but no appreciable solid solution formation had occurred at 400° after 100 hours.[73] The equilibrium constant of the reciprocal salt pair potassium bromide–sodium chloride, in the fused state at 769°, is 1·75.[73a]

TABLE XVII. CONDUCTIVITY, AND VISCOSITY, OF MOLTEN POTASSIUM BROMIDE–SILVER BROMIDE MIXTURES

Mol. Fraction, KBr.	t°C									
	350		400		450		500		550	
	κ	η	κ	η	κ	η	κ	η	κ	η
0	–	–	–	–	2·904	3·26	3·026	2·83	3·124	2·51
0·149	1·816	–	1·975	–	2·114	–	2·232	–	2·328	–
0·203	–	4·44	–	3·55	–	2·90	–	2·46	–	2·12
0·308	1·256	4·64	1·420	3·55	1·572	2·86	1·698	2·40	1·802	2·05
0·448	–	–	–	–	–	2·86	–	2·35	–	1·98
0·493	–	–	–	–	–	–	1·290	–	1·424	–
0·543	–	–	–	–	–	–	–	–	– –	2·04
0·591	–	–	–	–	–	–	–	–	1·304	–

	575		600		E_a, kg.-cal./mol.
0	κ	η	κ	η	
0	3·168	2·38	3·210	2·27	3·1
0·149	2·380	–	2·428	–	–
0·203	–	1·98	–	1·86	3·8
0·308	1·854	1·91	1·906	1·78	4·1
0·448	–	1·85	–	1·74	4·2
0·493	1·486	–	1·546	–	–
0·543	–	1·87	–	1·73	4·5
0·591	1·374	–	1·428	–	–

TABLE XVIII.- MOLAR MAGNETIC SUSCEPTIBILITIES OF POTASSIUM BROMIDE–SODIUM BROMIDE SOLID SOLUTIONS

Mol.-% KBr	$-10^7\chi_M$	Mol.-% KBr	$-10^7\chi_M$
10	388·7	65	432·0
35	414·2	70	434·1
40	417·5	80	437·2
50	427·7	100	440·4

TABLE XIX.- MOLAR MAGNETIC SUSCEPTIBILITIES OF POTASSIUM BROMIDE–POTASSIUM CHLORIDE SOLID SOLUTIONS

Mol.-% KBr	$-10^7\chi_M$	Mol.-% KBr	$-10^7\chi_M$
10	381·1	70	428·3
35	395·7	80	431·7
50	408·8	90	434·9
65	422·9	100	440·4

The refractive indices of dilute aqueous solutions of potassium bromide have been measured, and the molar refraction of the solute calculated, using the helium yellow line. The results are recorded in Tables XX and XXI.[74]

The refractive indices of more concentrated solutions of potassium bromide in water are recorded in Table XXII.[75]

TABLE XX.- THE REFRACTIVE INDICES OF SOLUTIONS OF POTASSIUM BROMIDE

Molarity, *m*.	t°	$10^6\delta n$*	$(\delta n/m)_{23}$	$n_{\text{soln.}}$
0·00107	23	14·7	0·01375	1·3327
0·00599	23·2	85·5	0·01428	1·3328
0·01006	23·1	141·9	0·01411	1·3329
0·05000	23	697·9	0·01396	1·3334
0·09990	22·8	1396·5	0·01397	1·3341

*δ is ($n_{\text{solution}} - n_{\text{water}}$ at t°C.

TABLE XXI.- MOLAR REFRACTION OF POTASSIUM BROMIDE, IN AQUEOUS SOLUTION, AT 25°C.

Molarity	$[R]_{\text{He}}$	Molarity	$[R]_{\text{He}}$
0	14·73	0·08	14·85
0·02	14·79	0·10	14·87
0·04	14·82	0·12	14·88
0·06	14·84		

TABLE XXII.- THE REFRACTIVE INDICES, AND MOLAR REFRACTION, OF POTASSIUM BROMIDE AT 25°C.

Molality	Density	n_{D}	$[R]_{\text{D}}$
0	0·99707	1·33266	14·925
1·4872	1·11409	1·35158	14·888
2·3613	1·17601	1·36133	14·863
3·2144	1·23229	1·37008	14·843
4·0556	1·28410	1·37803	14·823
5·1138	1·34473	1·38721	14·795

The temperature variation of $[R]_{\text{D}}$ over the range 6° - 30°, is $8{\cdot}0 \times 10^{-3}$.[76]

The densities of aqueous solutions of potassium bromide have been measured, with the results shown in Table XXIII.

TABLE XXIII.- DENSITIES OF AQUEOUS SOLUTIONS OF POTASSIUM BROMIDE

Molality	t°C.	d_4^t	Ref.
0	18	0·99862	78
0·0159	18	0·99999	78
0·0351	18	1·00106	78
0·0685	18	1·00447	78
0·1105	18	1·00798	78
4·409	15	1·3597	79
4·540	0	1·3237	77
4·573	20	1·3701	79
4·718	25	1·3794	79
6·23	35	1·3941	77
6·86	50·2	1·4160	77
8·53	91·95	1·4597	77

The relative supersaturation, λ, for aqueous solutions of potassium bromide, defined by:-

$$\lambda = \frac{c - c_0}{c_0}$$

where c is the concentration of the supersaturated solution, and c_0 the equilibrium solubility at that temperature, has been measured. λ has also been calculated, using the relationship:-

$$\lambda = A\exp.\ (\beta/T)$$

where β is a function of temperature T. The values obtained,[80] at 20°, are:-

$$\lambda_{calc.} = 0{\cdot}094$$

$$\lambda_{expt.} = 0{\cdot}056$$

The critical temperatures of potassium bromide solutions in water have been measured, and are listed in Table XXIV.[81]

TABLE XXIV.- THE CRITICAL TEMPERATURES OF AQUEOUS SOLUTIONS OF POTASSIUM BROMIDE

Molarity	$t°C._c$ (Solution)	$\delta t°C._{salt}$
0	374·3	–
0·04275	379·6	5·3
0·0850	383·0	8·7
0·171	389·4	15·2
0·343	399·4	25·2

The partial molal volumes of aqueous solutions of potassium bromide at 25° have been measured with the results given in Table XXV.[82]

TABLE XXV.- THE PARTIAL MOLAL VOLUMES OF AQUEOUS SOLUTIONS OF POTASSIUM BROMIDE

Molarity	V	Molarity	V
0	33·97	0·36	35·64
0·04	34·52	0·64	36·20
0·16	35·08	1·01	36·72

Then radii of the ions K^+ and Br^- have been calculated by extrapolation from the limiting volume occupied by the salt in saturated solution, to the hypothetical state where no water is present.[83] On this basis $r_{K^+} = 1{\cdot}59$A, and $r_{Br^-} = 2{\cdot}31$A.

The volume expansion of aqueous solutions of potassium bromide is recorded in Table XXVI.[84]

TABLE XXVI.- VOLUME EXPANSION, $10^5 \times \delta V/\delta T$, AS FUNCTION OF TEMPERATURE, AND WEIGHT FRACTION OF POTASSIUM BROMIDE (x_2)

x_2	0	0·05721	0·10465	0·20357	0·29858	0·38908
$t°C.$						
20	−116	−131	−141	−153	−157	−154
25	0	0	0	0	0	0
30	141	151	157	164	165	160
35	304	320	329	338	334	322
40	488	505	514	521	512	–
V_{25}	0	0·96237	0·92922	0·86112	0·79680	0·73655

The quantity V refers to the specific volume of the solution.

The apparent partial molal heat capacities of potassium bromide in aqueous solution have been evaluated.[85] At 25°, extrapolation to infinite dilution gives −29·5g.-cal./mole; its rate of change with temperature is 0·3g.-cal./mole-degree over the range 18° to 25°.

The apparent molal heat capacity of potassium bromide may be calculated from the equations:-[86]

$$\phi_{C_p} = -38{\cdot}167 + 20{\cdot}460\, m^{\frac{1}{2}} - 2{\cdot}645m, \text{ at } 25°, \text{ and}$$

$$\phi_{C_p} = -31{\cdot}135 + 14{\cdot}111m^{\frac{1}{2}} - 1{\cdot}133m, \text{ at } 30°$$

Heat data for aqueous solutions of potassium bromide are recorded in the following Tables, XXVII – XXXI.

TABLE XXVII. HEATS OF SOLUTION AND DILUTION, FOR AQUEOUS SOLUTIONS OF POTASSIUM BROMIDE AT 25°. EXTRAPOLATED TO INFINITE DILUTION.[87]

Integral heat of solution	−3·94kg.-cal./mole
Differential heat of solution	−3·31kg.-cal./mole
Differential heat of dilution	−64·5g.-cal./mole water

TABLE XXVIII.- INTEGRAL HEAT OF DILUTION AND PARTIAL MOLAL HEAT CONTENT, AT 25°C.[88]

Molality	Integral heat of dilution g.-cal./mole	Molality	Partial molal heat content g.-cal./mole
0	0	0	0
0·0001	−3·5	0·001	9
0·0004	−7·0	0·005	30
0·0016	−14·8	0·01	46
0·01	−34·0	0·05	71
0·04	−52·8	0·10	68
0·16	−61·9	0·20	37
0·25	−52·0	0·50	−91
0·64	23·5	1·0	−311
1·0	106	2·0	−680
2·25	353	3·0	−958
4·0	633	4·0	−1183
5·68*	841	5·0	−1347
		5·68*	−1414

* saturated solution

TABLE XXIX.- HEAT OF FORMATION OF AQUEOUS SOLUTIONS OF POTASSIUM BROMIDE[89] (see also Fig. 8)

Molecules water, per molecule KBr	$-\Delta H_f$, g.-cal.	t°C.
25	5096	23·5
100	5450	10·6
100	4809	23·5
200	5024	23·5
200	5080	23·5
400	5122	23·5

The integral heat of dilution of potassium bromide is recorded in Table XXX.[90]

The integral heat of dilution has also been measured in deuterium oxide-water solutions of potassium bromide, close to 100 mol % D_2O; these results are given in Table XXXI.[91]

The integral free energies of solution are reported in Table XXXII.[92]

The heat of hydration of potassium bromide is 152kg.-cal./mole.[93] The assumption of equal heats of hydration of K^+ ions and F^- ions, made by Bernal and Fowler[94] is rejected, the authors choosing $\Delta H_h\,(Cs^+)$ equal to $\Delta H_h\,(I^-)$; on this basis, they arrive at the individiual heats of hydration:-

$$\Delta H_h\ (K^+) = 80\text{kg.-cal./mole}$$

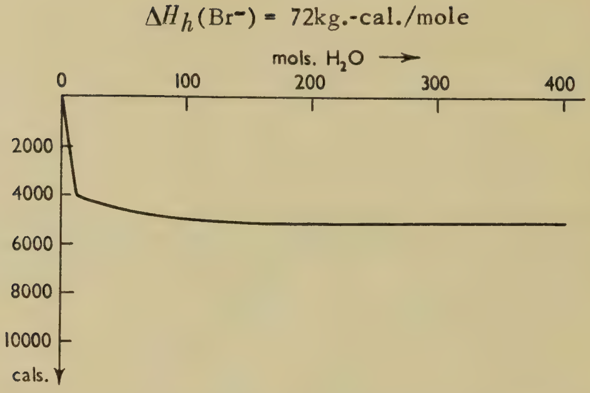


FIG. 8. THE HEAT OF SOLUTION OF POTASSIUM BROMIDE

TABLE XXX.- INTEGRAL HEAT OF DILUTION OF POTASSIUM BROMIDE IN AQUEOUS SOLUTION, AT 25°C.

Molal		$-\Delta H_d$, joules
Initial	Final	
2·80320	0·25258	896
1·03486	0·10048	602
0·51048	0·050184	84
0·10048	0·010021	79
0·050184	0·005009	41
0·010021	0·001001	37

TABLE XXXI.- INTEGRAL HEAT OF DILUTION OF SOLUTIONS OF POTASSIUM BROMIDE IN DEUTERIUM OXIDE, AT 25°C.

Mol.-% D_2O in D_2O/H_2O	Mol.-% Salt		Integral heat of diln.g.-cal./mole
	Initial	Final	
95·7	8·12	3·50	−409·0
95·5	3·51	1·35	−293·0
95·5	6·325	1·30	−613·0
95·4	4·9	1·35	−466·0
95·3	1·35	1·27	−149·0

TABLE XXXII.- INTEGRAL FREE ENERGIES OF SOLUTION OF POTASSIUM BROMIDE IN WATER, AT 25°C.

Molal	$-\Delta G^\circ$	Molal	$-\Delta G^\circ$
0·2	493	3·0	197
0·5	388	3·5	180
1·0	317	4·0	165
1·5	273	4·5	152
2·0	242	5·0	137
2·5	216	5·66*	118

* saturated solution

The hydration number for the bromide ion in aqueous potassium bromide at infinite dilution is 3·5;[95] hydration increases with decreasing volume of the alkali metal along the series potassium, sodium, and lithium bromides.[95a]

An equation proposed for the evaluation of standard free energies of hydration of alkali halides gives for potassium bromide the value 145·7kg.-cal./mole.[96] The calculation is based on thermodynamic data from the literature.

An equation has been proposed for the relative viscosity, η, of aqueous solutions of potassium bromide at 25°C as a function of their molar concentration:-

$$\eta_{\mathrm{KBr\ soln.}} = 1 + 0{\cdot}00474\sqrt{c} - 0{\cdot}04904c + 0{\cdot}01221c^2$$

At low concentrations, $\eta_{\mathrm{KBr\ soln.}} > \eta_{\mathrm{water}}$; at moderate concentrations, $\eta_{\mathrm{KBr\ soln.}} < \eta_{\mathrm{water}}$; minimum viscosity occurs at 1·9 molar concentration. The equation gives a maximum deviation of 0·01%, at concentrations up to 2 molar.[97] At 0°C, the equation becomes:-[98]

$$\eta_{\mathrm{KBr\ soln.}} = 1 + 0{\cdot}0045\sqrt{c} - 0{\cdot}15377c, \text{ up to } c \doteq 0{\cdot}05 \text{ molar}$$

An equation for the viscosity of potassium bromide solutions in water:-

$$\log\eta = \alpha + \beta/T$$

has been investigated over the range of concentration 0·14 to 0·84 molar. T in this equation is the absolute temperature, and α and β are constants, dependent upon concentration. The intersection of the curves at $T = 302{\cdot}4°$ indicates independence of concentration at this temperature.[99] Linearity of the graph of log η against $1/T°$ has been observed for aqueous solutions of potassium bromide, and of other alkali halides; no break occurs at the point of saturation.[100]

This form of the viscosity–temperature equation is due to Andrade.[100a]

The surface tensions of aqueous solutions of potassium bromide have been measured, and the results are recorded in Table XXXIII.

TABLE XXXIII.- SURFACE TENSIONS OF AQUEOUS SOLUTIONS OF POTASSIUM BROMIDE

g. KBr per 100 g. soln.	t°C.	Surface tension, dyne/cm.	
		$\gamma_{t°\mathrm{C.}}$	γ_{18}
0	18·5	72·58	72·65
6·97	19·3	73·04	73·62
14·45	17·6	74·42	74·37
21·19	16·8	75·81	75·63
28·39	17·8	77·04	77·00

The following relationships have been established, for aqueous solutions of potassium bromide:-

$$\eta = 200\,\beta, \text{ where } \beta \text{ is the adiabatic compressibility}$$

$$\gamma = 1{\cdot}2 \times 10^{-6}\,\rho v^{3/2}$$

where ρ is the density, v the ultrasonic velocity, η is the viscosity, and γ the surface tension.

The results of this investigation are given in Table XXXIV.[102]

The concentration dependence of the surface tension, γ, of aqueous potassium bromide solutions has been studied by the loop method.[103] For a number of strong electrolytes, the equation:-

$$\Delta\gamma = 0{\cdot}2437\alpha A + (\beta/2)A^2$$

has been established, where A is the activity of the solution, and α and β are constants specific to the electrolyte. For potassium bromide, $\alpha = 10{\cdot}2449$, $\beta/2 = 3{\cdot}4581$, and the equation is accurate to 0·3 molar concentration.

The interfacial tension, γ, between mercury and a molar aqueous solution of potassium bromide has been found to be 318·5ergs/cm.^{2}, taking γ_{Hg/H_2O} = 375·0.[104] The interfacial tension has also been measured between *n*-hexane and aqueous solutions of potassium bromide, with the results shown in Table XXXV.[105]

TABLE XXXIV.- VISCOSITY, η, AND SURFACE TENSION, γ, OF AQUEOUS SOLUTIONS OF POTASSIUM BROMIDE, AT 29°C.

Molar	Density	ν(metres)	$10^6\beta$	$\eta/10^3$	γ
0·1	1·005	1541	41·96	8·079	73·98
0·2	1·015	1534	42·37	8·364	75·77
0·3	1·023	1526	42·47	8·874	–
0·4	1·029	1532	41·88	8·925	77·59
0·5	1·040	1545	40·71	8·572	77·41
1·0	1·078	1547	39·18	8·668	77·23

TABLE XXXV.- THE INTERFACIAL TENSIONS OF *n*-HEXANE AND SOLUTIONS OF POTASSIUM BROMIDE, AT 20°C.

Molar	Surface tension, dyne/cm.	Interfacial tension, dyne/cm.
0·01	71·8	–
0·05	71·9	47·8
0·10	72·0	47·9
0·20	72·1	48·0
0·30	72·2	48·1
0	71·7	–

The boiling point elevation of aqueous solutions of potassium bromide has been measured at various concentrations, and the partial molal free energies calculated[106] with the results given in Table XXXVI.

TABLE XXXVI.- BOILING POINT ELEVATION, AND PARTIAL MOLAL FREE ENERGY OF VAPORISATION, OF AQUEOUS SOLUTIONS OF POTASSIUM BROMIDE

Molarity	Δb.p. at 100°C.	$-\Delta G_1$
0·1	0·0944	10·28
0·2	0·1868	20·34
0·3	0·2794	30·41
0·4	0·3723	40·51
0·5	0·4657	50·66
1·0	0·9453	102·08
1·5	1·447	156·9
2·0	1·970	213·4
3·0	3·081	332·5
4·0	4·276	459·7
5·0	5·563	–

The molecular weight of potassium bromide, calculated from the boiling point elevation of the most dilute solution measured, was 66·0; the value fell to 55·7, for a solution of 51·2 g. of potassium bromide in 100g. of water.[107]

The freezing points of aqueous potassium bromide solutions have been redetermined, and the mean ion activity coefficients derived; it was observed that deviations were greater for bromides than for chlorides, and increased along the series K – Na – Li, with a common anion.[108] In Table XXXVII, the results are recorded; j is defined as $(1 - \theta/3{\cdot}716M)$, where M is the molality, and θ the freezing point depression, and $\gamma\pm$ is the mean ion activity coefficient.

From the boiling point elevation, it has been estimated that, at 107° the hydration of potassium bromide corresponds to $KBr,6H_2O$.[109] Freezing point data yield the values 8·1 H_2O, in molar solution, and 9·6 H_2O in 0·5 molar solution.[110]

TABLE XXXVII.- FREEZING POINT DEPRESSION, AND ACTIVITY COEFFICIENTS, OF POTASSIUM BROMIDE, IN AQUEOUS SOLUTION

Molality, m	j	$-\log \gamma\pm$, molal	m	j	$-\log \gamma\pm$, molal
0·001	0·0111	0·0148	0·30	0·0950	0·1590
0·002	0·0152	0·0205	0·40	0·1012	0·1737
0·005	0·0230	0·0313	0·50	0·1056	0·1855
0·01	0·0309	0·0428	0·60	0·1090	0·1955
0·02	0·0407	0·0578	0·70	0·1117	0·2038
0·05	0·0567	0·0839	0·80	0·1138	0·2111
0·10	0·0707	0·1091	0·90	0·1157	0·2177
0·20	0·0860	0·1392	1·0	0·1173	0·2236
—	—	—	1·10	0·1187	0·2290

Hydration studies employing the ultrasonic interferometer lead to values for the volume of hydration water at various concentrations of electrolyte solutions. The values for aqueous solutions of potassium bromide are recorded in Table XXXVIII.[111]

TABLE XXXVIII.- VOLUME OF HYDRATION WATER, IN POTASSIUM BROMIDE SOLUTIONS

Molarity	Wave-length, mm.	V, c.c./mole
3·3610	1·0961	31·82
2·0166	1·0955	42·11
1·0083	1·0926	52·88
0·6050	1·0885	57·32
0·2017	1·0857	63·48

Limiting value at infinite dilution, V = 75 c.c./mole, as compared with the earlier value of 81 c.c./mole.[112]

The electrical conductivity of aqueous solutions of potassium bromide has been measured, with the results shown in Tables XXXIX to XLIII.

TABLE XXXIX.- CONDUCTIVITY FUNCTION (M/κ) FOR AQUEOUS SOLUTIONS OF POTASSIUM BROMIDE AT 10°C.[113]

Molality, M	M/κ	Molality, M	M/κ
0·001469	9·316	0·19939	10·452
0·005370	9·420	0·28251	10·677
0·014042	9·551	0·46754	11·073
0·020343	9·620	0·72135	11·497
0·046983	9·829	1·07251	11·962
0·096075	10·085	1·29601	12·216

κ is the specific conductivity, in $ohm^{-1}cm.^{-1}$

From the results given in Table XLIII, heats of dissociation of potassium bromide were determined:-

$$0° \text{ to } 18°,\ \Delta H_{\text{dissocn.}} = 5413 \text{g.-cal./mole}$$

$$18° \text{ to } 25°,\ \Delta H_{\text{dissocn.}} = 9752 \text{g.-cal./mole}$$

The activity coefficients of alkali halides have been obtained from the study of cells of the type:-

$$\mathrm{Ag, AgX} \mid \mathrm{MX_m} \mid \mathrm{M\,Hg} \mid \mathrm{MX_{0\cdot1}} \mid \mathrm{AgX, Ag}$$

where M is the alkali metal, and X the halide ion. The electromotive force of this cell may be expressed:-

$$E = 0{\cdot}1183 \cdot \log \frac{\gamma_m \cdot m}{\gamma_{0\cdot1} \cdot 0{\cdot}1}$$

TABLE XL.- EQUIVALENT CONDUCTIVITY OF POTASSIUM BROMIDE, IN AQUEOUS SOLUTIONS, AND THE LIMITING MOBILITY, λ, OF THE BROMIDE ION[114]

10^4 molar	0	5	10	20	50	100
t°C. = 15°	122·84	121·22	120·57	119·69	118·02	116·30
25°	151·67	149·60	148·78	147·64	145·49	143·23
35°	182·32	179·76	178·74	177·34	174·70	171·94
45°	214·18	211·07	209·84	208·13	204·91	201·53
t°C.	λ° (Br)	$d\ln\lambda^\circ/dt$				
15°	63·17	0·0231				
25°	78·15	0·0199				
35°	94·07	0·0173				
45°	110·65	0·0153				

TABLE XLI.- EQUIVALENT CONDUCTIVITY, Λ, OF AQUEOUS POTASSIUM BROMIDE SOLUTIONS[115]

$10^3\,c$	Λ_5	δ	$10^3\,c$	Λ_{25}	δ	$10^3\,c$	Λ_{55}	δ
0	96·00	–	0	151·68	–	0	247·15	–
1·1480	94·13	0	1·3949	148·27	−1	1·2891	241·37	−5
2·2559	93·41	0	2·7881	146·91	+1	2·6802	238·86	+3
3·8367	92·68	−1	4·2183	145·88	+2	4·2678	236·85	+5
6·0580	91·90	0	5·9269	144·90	+1	7·0329	234·21	+4
7·5932	91·47	−1	7·1696	144·30	−1	8·8795	232·80	+2
–	–	–	–	–	–	11·0850	231·35	0
–	–	–	–	–	–	13·2244	230·16	−7

c = concentration in g.equivalents/litre
δ = 100(Λ°C. calc. − Λ°C. obs.)

TABLE XLII.- MOLAR CONDUCTIVITY, Λ, AND MEAN ION ACTIVITY COEFFICIENT $f_\pm$, OF POTASSIUM BROMIDE, IN AQUEOUS SOLUTION, AT 25°C.[116]

c	Λ	$f_\pm$
0·05	135·7	0·887
0·01	144·4	0·942
0·002	148·5	0·970
0	153·0	–

TABLE XLIII.- SPECIFIC CONDUCTANCE OF POTASSIUM BROMIDE SOLUTIONS[117]

Molar	$\kappa_{0^\circ\mathrm{C.}}$	κ 0°C.
0·1	$70{\cdot}9 \times 10^{-6}$	$226{\cdot}3 \times 10^{-4}$
0·01	$88{\cdot}1 \times 10^{-6}$	$230{\cdot}6 \times 10^{-4}$
0·001	$72{\cdot}6 \times 10^{-6}$	$231{\cdot}3 \times 10^{-4}$

The results for potassium bromide solutions are given in Table XLIV. Good agreement is obtained with the results of other calculations.[118]

TABLE XLIV.- MEAN ION ACTIVITY COEFFICIENTS OF POTASSIUM BROMIDE, IN AQUEOUS SOLUTION AT 25°C.

Molarity	$\gamma_m/\gamma_{0.1}$	$\gamma\pm$
0·05	1·064	0·816
0·10	1·000	0·768
0·30	0·905	0·695
0·50	0·855	0·656
1·0	0·799	0·613
1·5	0·784	0·602
2·0	0·778	0·598
2·5	0·787	0·604

The activities of the components, in saturated solutions containing potassium bromide and potassium chloride, have been measured;[119] the results are given in Table XLV.

TABLE XLV.- ACTIVITIES OF SOLUTES, IN THE SYSTEM $H_2O/KBr/KCl$, AT 25°C.

Solid phase mol.-fraction KBr	Liquid phase, molalities		a_{KCl}	a_{KBr}
	KBr	KCl		
0·000	0	4·819	2·93	0
0·049	1·087	4·14	2·84	1·50
0·128	2·237	3·472	2·70	2·31
0·177	2·649	3·248	2·65	2·59
0·376	3·252	2·848	2·52	2·96
0·436	3·406	2·707	2·45	3·04
0·677	3·816	2·304	2·25	3·24
0·806	4·407	1·674	1·89	3·49
0·874	4·916	1·135	1·54	3·69
0·939	5·231	0·728	1·22	3·79
1·000	5·753	0	0	3·91

The transport number of the potassium ion, in aqueous solutions of potassium bromide, has been measured by the Hittorf method (Table XLVI), and by the moving-boundary method (Table XLVII).

TABLE XLVI.- CATION TRANSPORT NUMBER FOR POTASSIUM BROMIDE SOLUTIONS, BY THE HITTORF METHOD[120]

Molality	t = 25°C.	30°C.	35°C.
0·101	0·495	0·496	0·496
0·511	0·495	0·495	0·496
1·035	0·491	0·492	0·493
2·803	0·485	0·486	0·489

A comparison of transport and conductivity data for potassium bromide and potassium chloride, in 0·1 N. solution, at 25°, gave the following results:-[122]

	Λ	t^+	η	$t^+.\Lambda$	$t^+\Lambda\eta$
KBr	131·6	0·485	0·9946	63·8	63·5
KCl	129·0	0·492	0·9982	63·5	63·4

where Λ is the equivalent conductivity of the solution, t^+ the transport number of the cation, and η the viscosity.

A very accurate moving boundary investigation gave the following results for the cation transport numbers in aqueous solutions of potassium bromide, at

25°: c is the molarity of the solution:-[123]

c	0·01	0·02	0·05	0·10	0·20
t^+	0·4833	0·4832	0·4831	0·4833	0·4841

so that a minimum in t_{K^+} appears to be well established.

TABLE XLVII.- CATION TRANSPORT NUMBER, t^+, AND MOBILITY, λ^+, IN AQUEOUS POTASSIUM BROMIDE SOLUTIONS, AT 25°C.[121]

Molality	t^+	λ^+	Molality	t^+
0	0·4847	73·52	–	–
0·0005	0·4846	72·50	0·02	0·4838
0·001	0·4845	72·08	0·03	0·4837
0·002	0·4844	71·52	0·05	0·4838
0·005	0·4843	70·46	0·07	0·4843
0·010	0·4841	69·35	0·10	0·4852

From measurements of liquid junction potentials in electromotive force cells, the average potential difference for potassium bromide salt bridges was found to be:-[124]

4 Molar, 0·43 m.V.; saturated, 0·50 m.V.

The Soret coefficient for potassium bromide has been calculated;[125] by taking the data of Goodrich,[126] the value $+3{\cdot}9 \times 10^{-3}$ is obtained, but the Soret coefficient depends upon temperature, and with a temperature difference of 17° between vessels, the following results were obtained:-[127]

$t°$	30°	40°	50°	60°
$10^3 \cdot \sigma_{KBr}$	1·12	2·25	2·76	3·48

The adsorption of potassium bromide on barium sulphate,[128] and on lead sulphide,[129] has been studied, as part of a more extended survey of the adsorption of electrolytes upon such precipitates.

The molar refractivity, dispersivity, and rotativity, of aqueous solutions of potassium bromide, at 25°, for magneto-optic rotation and dispersion, have been measured, and are listed in Table XLVIII.[130]

TABLE XLVIII.- MOLAR REFRACTIVITY, $[R]_m$, MOLAR DISPERSIVITY, $[D]_m$, AND MOLAR ROTATIVITY, $[\Omega]_m$, FOR AQUEOUS SOLUTIONS OF POTASSIUM BROMIDE, AT 25°C.

Molarity	$[R]_m$	$[D]_m$	$[\Omega]_m$
1·0	15·39	46·7	23·70
3·0	15·24	45·0	21·95
4·0	15·14	44·2	21·20

$\lambda = 5461$ A.

The magnetic susceptibility, χ_m, for potassium bromide in aqueous solution, is $50{\cdot}3 \times 10^{-6}$, at 20°.[131]

Compressibilities of aqueous solutions of potassium bromide are recorded in Table XLIX.[132]

The solubility of potassium bromide in water at 32·4° is 725·6 g. per 1000 g. of water. The increased solubility of potassium bromide in bromine water is one-third of the bromine concentration, up to 382·1 g. of bromine per 1000 g. of water: so that 1000 g. of water + 382·1 g. of bromine dissolves 845·9 g. of potassium bromide. The salt is quite insoluble in liquid bromine.[133]

In a study of potassium bromide in non-aqueous solution, its solubility in liquid ammonia has been determined. At −33·9°, 40·32 g. of the salt dissolve in 100 g. of ammonia:[134] at 0°, the solubility is 26·9 g. per 100 g. of ammonia.[135]

TABLE XLIX.- THE COMPRESSIBILITIES AND SPECIFIC VOLUMES OF AQUEOUS SOLUTIONS OF POTASSIUM BROMIDE, OVER A PRESSURE RANGE OF 1 TO 1000 BARS, AT 25°C.

$100x_2$	$10^4 k$	v	$\frac{-\Delta P v}{x_1} 10^4$	Deviation
0	393·5	1·0029	394·6	–
8·26	369·4	0·9446	380·3	−0·1
13·79	353·1	0·9063	371·2	+0·2
20·00	334·9	0·8636	361·5	0·8
26·47	317·2	0·8196	353·6	−0·1
32·88	299·1	0·7762	345·9	−0·3
39·02	281·7	0·7354	339·8	−0·6

x_2 = Wt. fraction of salt, in solution.

k = Decrease in volume, per unit volume. } over the pressure

$-\Delta P v$ = Specific compression of solution. } range 1 - 1000 bars

V = Specific volume of solution.

Deviation = $10^4(A_{\text{obs.}} - A_{\text{calc.}})$ where

$$A_{\text{obs.}} = \frac{-\Delta P v}{x_1} 10^4$$

$$A_{\text{calc.}} = r_2(a + b c_2^{1/2})$$

in which $r_2 = \dfrac{\text{Wt. fraction of salt in solution.}}{\text{Wt. fraction of water in solution.}}$

c_2 = Concn. of salt in soln., g./c.c.

$10^4 a = 212·4$ } for KBr solutions.

$-10^4 b = 172·8$ }

The decomposition potential of potassium bromide in liquid ammonia solution has been measured; it varies slightly according to the electrode materials:[136] E_d = 3·45 volts, with platinum electrodes for a 22% KBr solution; E_d = 3·60 volts with carbon anode and iron cathode, also for 22% KBr solution.

In the same investigation, the solubility of potassium bromide in liquid ammonia was measured, and the nature of the solid phase in equilibrium determined; the results are given in Table L.

TABLE L.- SOLUBILITY OF POTASSIUM BROMIDE IN LIQUID AMMONIA[136]

t°C.	Wt.-% KBr	Solid Phase	t°C.	Wt.-% KBr	Solid Phase
−77·7	0	NH_3	−83	11·54	$KBr,4NH_3$
−78·0	2·43	NH_3	−82	12·45	$KBr,4NH_3$
−78·5	4·18	NH_3	−80	14·32	$KBr,4NH_3$
−79·0	5·99	NH_3	−75·5	16·66	$KBr,4NH_3$
−79·5	6·69	NH_3	−75·0	17·16	$KBr,4NH_3$
−80·0	7·37	NH_3	−59·0	25·43	$KBr,4NH_3$
−84·0	11·0	$NH_3 + KBr,4NH_3$	−58·0	27·0	$KBr,4NH_3 + KBr$
–	–	–	−51·5	25·43	KBr
−47·5	25	KBr	+21·5	11·48	KBr
−42	22·23	KBr	22·3	11·66	KBr
−36	22·86	KBr	25	11·8	KBr

continued on following page

TABLE L.- CONTINUED.

t°C.	Wt.-% KBr	Solid Phase	t°C.	Wt.-% KBr	Solid Phase
−34	22·08	KBr	25	11·89	KBr
−26	21·09	KBr	35	8·14	KBr
−16	17·18	KBr	36	7·26	KBr
−10	16·98	KBr	42·5	6·92	KBr
−7	17·16	KBr	43·5	6·00	KBr
−4·5	16·66	KBr	55·8	4·26	KBr
+0·1	21·18	KBr	65	2·51	KBr
5·0	14·80	KBr	77	1·61	KBr
5·0	14·32	KBr	98	0·865	KBr

The heat of solution of potassium bromide in liquid ammonia is 2·90kg.-cal./mole, at −33°,[137] and the heat of the "neutralisation" reaction, NH_4Br + KNH_2,am. = KBr,am. + $2NH_3$ (liq)., is −27·5kg.-cal./mole.[137]

Conductivity studies have been made of potassium bromide solutions in anhydrous hydrazine; the solvent had the following specific conductivity:-

$$\kappa_{0°C.} = 1·1 \text{ to } 2·0 \times 10^{-6}$$
$$\kappa_{25°C.} = 2·3 \text{ to } 2·8 \times 10^{-6}$$

Conductivities are recorded in Table LI, together with calculated values from the equation:-

$$\lambda = 134·9 - 158\sqrt{c}$$

TABLE LI.- EQUIVALENT CONDUCTIVITY, Λ, OF POTASSIUM BROMIDE IN ANHYDROUS HYDRAZINE, AT 25°C.[138]

10^4 c (molar)	$\Lambda_{obs.}$	$\Lambda_{calc.}$
13·03	128·9	129·2
20·56	127·6	127·7
58·82	122·7	122·8
96·47	119·9	119·4
120·7	118·1	117·5
165·4	116·1	–

Solutions of potassium bromide in iodine monobromide, IBr, show high conductivity. (The solvent had a melting point of 41° and a boiling point of 119°; specific conductivity at 55°, 3×10^{-4} ohm^{-1}cm^{-1}. Density at 42°, 3·76.)

The specific conductivity, κ, and equivalent conductivity, Λ, of solutions in this solvent, are recorded in Table LII.[139]

Electrolysis of potassium bromide solutions (8·4 and 9·7 mol % KBr) in iodine monobromide, at 40 – 45°, using platinum electrodes, gave the following transport number of the ions:-

$$t_{K^+} = 0·43, \ t_{I^-} = 0·17$$

It was also observed that the transport of bromine amounted to 1·51g.-atoms per Faraday. It was concluded that the complex $KIBr_2$ is formed when the molecular ratio IBr/KBr = 4·35 – 4·55, and that for each mole of $KIBr_2$ electrolysed, ½ mole of iodine monobromide is also electrolysed.[139a]

In molten aluminium bromide, at 110°, potassium bromide forms a complex anion, as shown by the transport number, 1·14, for the cation.[140]

The equivalent conductivity of potassium bromide dissolved in fused antimony trichloride, at concentrations up to 2M. is recorded in Table LIII.[141]

In the solvent phosphorus oxychloride, potassium bromide dissolves to the extent of 0·51g./1, and the specific conductivity of the saturated solution is $4·3 \times 10^{-5}$ohm^{-1}cm.$^{-1}$ at 20°. From the variation of equivalent conductivity with concentration, it is inferred that the salt is only slightly ionised in this solvent.[142]

The solubility of potassium bromide in methyl alcohol at various temperatures is recorded in Table LIV.[143]

TABLE LII.- ELECTRICAL CONDUCTIVITIES OF SOLUTIONS OF POTASSIUM BROMIDE IN IODINE MONOBROMIDE, AT 55°C.

Molarity	κ	Λ
0	$4·61 \times 10^{-4}$	–
0·0223	$2·44 \times 10^{-3}$	110
0·0562	$4·12 \times 10^{-3}$	73·2
0·0948	$5·61 \times 10^{-3}$	59·3
0·122	$6·80 \times 10^{-3}$	55·8
0·180	$9·11 \times 10^{-3}$	50·7
0·267	$13·1 \times 10^{-3}$	49·1
0·386	$18·6 \times 10^{-3}$	48·3
0·455	$21·5 \times 10^{-3}$	46·3
0·700	$32·2 \times 10^{-3}$	46·0
1·109	$40·1 \times 10^{-3}$	44·4

TABLE LIII.- EQUIVALENT CONDUCTIVITY OF POTASSIUM BROMIDE IN FUSED ANTIMONY TRICHLORIDE, AT 99°C.

Molarity	KBr	Molarity	KBr
0	159	0·02	129
0·0001	153	0·05	119
0·0005	149	0·10	111
0·001	147	0·50	85·1
0·005	139	1·0	66·5
0·01	134	2·0	40·7

TABLE LIV.- SOLUBILITY OF POTASSIUM BROMIDE IN METHYL ALCOHOL

t°C.	Soly. g./g. MeOH	t°C.	Soly. g./g. MeOH
0	0·0182	30	0·0223
10	0·0193	40	0·0237
15	0·0200	50	0·0255
20	0·0208	60	0·0274

The solubility has also been measured in methyl alcohol–water mixtures, with the results shown in Table LV.[144]

TABLE LV.- SOLUBILITY OF POTASSIUM BROMIDE IN METHYL ALCOHOL–WATER MIXTURES, AT 25°C.

Wt.-% MeOH	Mol. fraction MeOH	Solubility, moles per 1000 g. solvent
0	0	5·784
20·00	0·1233	3·711
40·82	0·2795	2·180
59·56	0·4530	1·1802
72·39	0·5959	0·7697
80·03	0·6927	0·4625
89·79	0·8311	0·2629
94·76	0·9103	0·2049
100·0	1·000	0·1805

The solubility of potassium bromide in ethylene glycol–water mixtures has been measured; the results[146] are given in Table LVI.

The solubilities of potassium bromide and potassium iodide have been measured at 10° and 20°, in aqueous methanol and aqueous ethanol.[145] The results are represented graphically in Figs. 9 and 10.

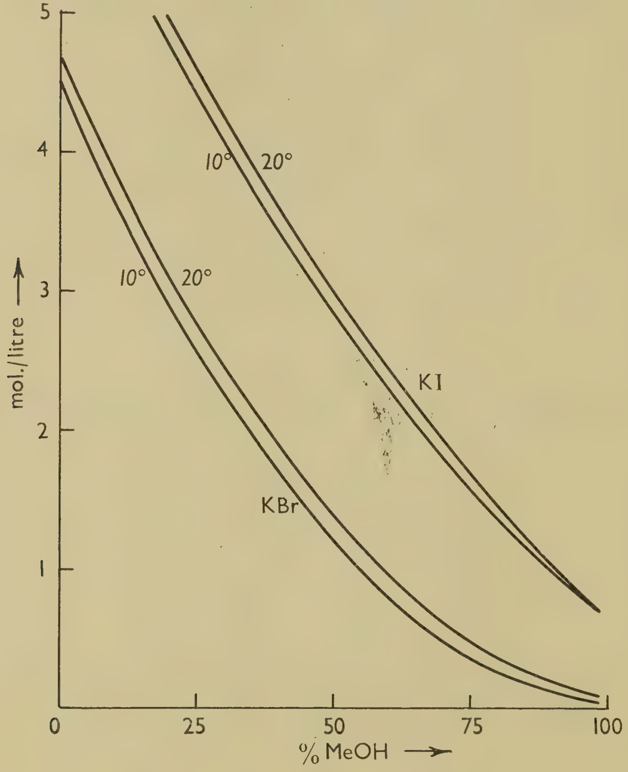


FIG. 9. SOLUBILITY OF KBr (AND KI) IN AQUEOUS METHANOL AT 10° AND 20°C

At 25° the solubility of potassium bromide in acetone is $3{\cdot}69 \times 10^{-4}$ molar, corresponding to an ionic strength of $3{\cdot}69 \times 10^{-4}$; the Debye–Huckel theory was found to apply to dilute solutions in acetone.[147]

The solubility of potassium bromide in acetone–water mixtures, relative to the solubility in water, is recorded in Table LVII.[148]

The solubilities of potassium bromide in methyl alcohol, acetonitrile, and formic acid have been measured at 18° and 25 °C.; the results are given in Table LVIII.[149]

The solubility of potassium bromide, and of other alkali halides, in solvents likely to be used in Soxhlet extraction, has been measured.[150] The logarithm of solubility varies linearly with the inverse of the dielectric constant for the following solvents at 25°: water, methyl alcohol, ethyl alcohol, propyl alcohol, amyl alcohol.[151]

The dissociation constant for potassium bromide[152] in 90% acetone at 25 °C. is $1{\cdot}3 \times 10^{-2}$.

The viscosities and densities of solutions of potassium bromide in anhydrous methyl alcohol are given in Table LIX.[153]

The surface tensions of the ternary solutions potassium bromide–ethyl alcohol–water, and potassium bromide–acetic acid–water, have been measured; the results are listed in Table LX.[154]

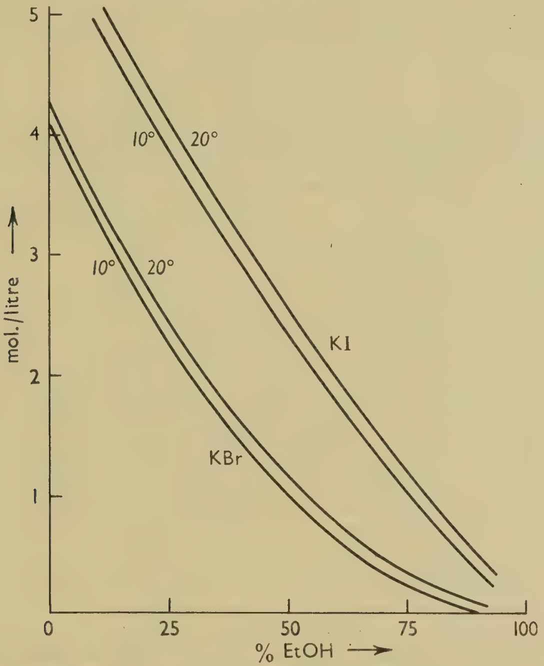


FIG. 10. SOLUBILITY OF KBr (AND KI) IN AQUEOUS ETHANOL AT 10° AND 20°C

TABLE LVI.- SOLUBILITY OF POTASSIUM BROMIDE IN ETHYLENE GLYCOL–WATER MIXTURES, AT 30°C.

% glycol	% water	% KBr	Density
0	58·42	41·58	1·3876
12·73	51·45	35·82	1·3417
28·29	42·07	29·64	1·2995
46·08	30·34	23·58	1·2637
65·67	16·30	18·03	1·2338
86·32	0	13·68	1·2131

TABLE LVII.- RELATIVE SOLUBILITY OF POTASSIUM BROMIDE IN ACETONE–WATER MIXTURES, AT 18°C.

% acetone	Relative Soly.	% acetone	Relative Soly.
0	1·0	50	0·67
10	0·95	60	0·58
20	0·88	70	0·48
30	0·82	80	0·35
40	0·76	–	–

The heat of solution of potassium bromide in methyl alcohol, at 20°, has been measured.[155] Extrapolation to infinite dilution gives −1·067kg.-cal./mole.

The equivalent conductivity of potassium bromide in acetic acid is recorded in Table LXI.[156]

From the data there given, the limiting equivalent conductivity was calculated by the method of Fuoss and Kraus [157] to be 41, and the ion-pair dissociation constant, $K \times 10'$, = 1·1.

The solubility of potassium bromide in acetic acid–sodium acetate mixtures has been measured. From the results have been deduced the equilibrium constant, K_1, for the exchange reaction:-

$$\mathrm{KBr + NaOAc \rightleftharpoons KOAc + NaBr}$$

and the ion-pair association constant, K_2, for the salts.[158]

TABLE LVIII.- SOLUBILITIES OF POTASSIUM BROMIDE IN ORGANIC SOLVENTS

Solvent	t°C.	Density	Solubility	
			g./100 g. solvent	mol./litre
Methyl Alcohol	18	0·805	1·99	0·132
	25	0·806	2·10	0·139
Acetonitrile	18	0·782	$2·3 \times 10^{-2}$	$1·5 \times 10^{-3}$
	25	0·777	$2·4 \times 10^{-2}$	$1·6 \times 10^{-3}$
Formic Acid	18	1·387	22·4	2·14
	25	1·380	22·7	2·15

TABLE LIX.- VISCOSITIES AND DENSITIES OF SOLUTIONS OF POTASSIUM BROMIDE IN METHYL ALCOHOL, AT 25°C.

Molality	Density	Viscosity, c.g.s. units
0·10884	0·79650	0·00576
0·09926	0·79490	0·00574
0·07192	0·79343	0·00567
0·04446	0·79027	0·00560
0·02840	0·78991	0·00554

TABLE LX.- SURFACE TENSIONS OF TERNARY SOLUTIONS OF POTASSIUM BROMIDE, AT 25°C.

<table>
<tr><th colspan="3">Ethyl Alcohol/Water, 2·03 mol.-% EtOH</th></tr>
<tr><th>molal KBr, <i>m</i></th><th>surface tension, γ</th><th>−dγ/d<i>m</i></th></tr>
<tr><td>0·99</td><td>54·75</td><td>0·86</td></tr>
<tr><td>1·97</td><td>54·35</td><td>0·40</td></tr>
<tr><td>2·95</td><td>54·19</td><td>0·16</td></tr>
<tr><th colspan="3">Acetic acid/Water, 0·353 mol.-% CH₃COOH</th></tr>
<tr><td>1·00</td><td>69·65</td><td rowspan="3">+dγ/d<i>m</i> = 0·99, over this range</td></tr>
<tr><td>2·00</td><td>70·56</td></tr>
<tr><td>3·00</td><td>71·44</td></tr>
</table>

TABLE LXI.- EQUIVALENT CONDUCTIVITY OF POTASSIUM BROMIDE IN ACETIC ACID, AT 30°C.

10^4 c, moles/l.	Λ_c	10^4 c, moles/l.	Λ_c
0·914	1·281	6·173	0·6006
2·247	1·150	9·614	0·4861
2·334	1·107	11·90	0·4422
3·525	0·908	13·32	0·4203
3·661	0·874	23·38	0·3420
4·498	0·6785	76·07	0·1954

The equivalent conductivities of potassium bromide in *n*-propyl alcohol and *iso*propyl alcohol, at 25°, have been determined, the results being given in

Table LXIII.[159]

TABLE LXII.- SOLUBILITY OF POTASSIUM BROMIDE IN ACETIC ACID–SODIUM ACETATE, AND CONSTANTS FOR THE EQUILIBRIA, AT 30°C.

Cocn., moles/100 moles Acetic Acid		K_1	K_2
NaOAc	KBr		
0·003307	0·02105	0·0123	0·0122
0·007700	0·02332	0·0089	0·0087
0·01007	0·02469	0·0107	0·0104
0·01997	0·02853	0·0105	0·0101
0·03231	0·03275	0·0115	0·0109
0·05742	0·03924	0·0119	0·0111
0·07169	0·04173	0·0113	0·0104
0·09575	0·04698	0·0122	0·0111
Average deviation,		0·0008	0·0006

TABLE LXIII.- EQUIVALENT CONDUCTIVITY OF POTASSIUM BROMIDE IN PROPYL ALCOHOLS, AT 25°C.

10^4 molar	Λ *n*-Propyl alcohol	$10^3 K_1$	$10^3 K_2$
1·303	20·98	1·283	2·434
1·732	20·53	1·326	2·263
4·760	18·57	1·642	2·284
7·190	17·60	1·822	2·389
Λ_0 = 23·54			
10^4 molar	Λ *iso*-Propyl alcohol	$10^3 K_1$	$10^3 K_2$
2·380	13·65	3·524	3·679
3·634	12·26	3·650	3·653
4·161	11·66	3·424	3·442
5·134	11·18	–	–
Λ_0 = 19·50			

In the above Tables K_1 is the dissociation constant, calculated from Ostwald's Dilution Law; K_2 is the dissociation constant calculated by the method of Fuoss and Kraus.[157]

Transport number determination by the moving boundary method, and the evaluation of limiting ionic mobilities, for potassium bromide solutions in methyl alcohol, gives the results listed in Table LXIV.

TABLE LXIV.- TRANSPORT NUMBER OF THE CATION, AND LIMITING IONIC MOBILITIES, FOR POTASSIUM BROMIDE IN METHYL ALCOHOL, AT 25°C.

10^3 *c* (molar)	t_{K^+}	$\lambda^\circ_{K^+}$	$\lambda^\circ_{Br^-}$	Ref.
9·606	0·4793	–	–	160
6·068	0·4790	–	–	160
3·890	0·4787	–	–	160
0	0·4795	–	–	160
0	–	52·40	56·55	161

The limiting values of the product $\lambda^\circ\eta$, where η is the viscosity at 25°, are:-[161]

$\lambda^\circ\eta_{K^+}$, 0·285

$\lambda^\circ\eta_{Br^-}$, 0·308

The equivalent conductivity of potassium bromide in dimethylformamide solution has been measured: the results are given in Table LXV. The observed $\Lambda/\sqrt{c}$ slope differs from the theoretical Onsager slope by 4%.[162]

TABLE LXV.- EQUIVALENT CONDUCTIVITY OF POTASSIUM BROMIDE IN DIMETHYLFORMAMIDE, AT 25°C.

10^4 molar	Λ	10^4 molar	Λ
0	84·1	13·32	78·5
0·730	82·8	22·94	76·7
3·614	81·4	37·66	74·8

The equivalent conductivity has also been measured in N-methylacetamide solution, at temperatures from 30° to 60°, as recorded in Table LXVI.[163]

TABLE LXVI.- EQUIVALENT CONDUCTIVITY OF POTASSIUM BROMIDE IN N-METHYLACETAMIDE

t°C.	Dielectric constant	Λ°	$\Lambda^\circ\eta$	Expt. slope	Onsager slope	Devn. %
30	179	16·6	0·645	10·8	10·1	+6
40	166	21·1	0·637	13·8	13·5	+2
50	152	26·2	0·632	17·1	17·4	−2
60	139	32·1	0·629	21·0	22·2	−5

Specific conductances in the same solvent have been measured over the temperature range 24° to 33°, with the results shown in Table LXVII.[164]

TABLE LXVII.- SPECIFIC CONDUCTIVITY OF POTASSIUM BROMIDE IN N-METHYLACETAMIDE

t°C.	$10^6\kappa$ ohm^{-1}cm.$^{-1}$	t°C.	$10^6\kappa$ ohm^{-1}cm.$^{-1}$
24	283	29	299
25	270	30	307
26	277	31	315
27	284	32	323
28	292	33	330

Melting point of solvent, 29·8°C.
Specific conductivity of solvent, $4{\cdot}2 \times 10^{-7}$ ohm^{-1}cm.$^{-1}$, at 35°C.

The equilibrium constant for the dissociation of potassium tribromide, KBr_3, in acetic acid, and the energy-change ΔE of the dissociation:-

$$KBr_3 \rightarrow KBr + Br_2$$

are listed in Table LXVIII.[165]

TABLE LXVIII.- EQUILIBRIUM CONSTANT, AND ENERGY CHANGE FOR THE DISSOCIATION OF KBr_3, IN ACETIC ACID

t°C.	10^2K, mole/l.	ΔE, g.-cal./mole
30	1·80	7110
50	3·67	6910
70	7·22	−

Chemical Properties

The following reaction occurs when potassium bromide is acted upon by sulphur trioxide. in vacuo, and at temperatures between 20° and 100°:-

$$2KBr + 4SO_3 = K_2S_3O_{10} + Br_2 + SO_2$$

X-Ray analysis of the products shows that only $K_2S_3O_{10}$ is formed; there is no trace of an intermediate such as $K_2S_2O_7$, nor are halogen-sulphonates formed (as from potassium fluoride and chloride). Potassium bromide gives an orange-red colour with even a trace of sulphur trioxide.[166]

Potassium bromide in aqueous solution reacts with oxygen, in the presence of mercury and activated charcoal, potassium hydroxide and mercuric bromide being formed.[167] The rate of the reaction increases with increase in temperature between 1° and 50°, but then decreases slightly, up to 85°. The rate is proportional to the amount of charcoal present, and to the oxygen content of the gas stream; it is inversely proportional to the concentration of the potassium bromide solution.

Ultrasonic irradiation of solutions of potassium bromide causes the liberation of bromine, partly owing to oxidation by the hydrogen peroxide also formed. The amount of bromine liberated from neutral solution decreases with increase in concentration of potassium bromide.[168]

Gaseous chlorine reacts with solid potassium bromide only if water vapour is present. Before appreciable interaction occurs a minimum partial pressure of water vapour must be attained, at each temperature, approximating to the vapour pressure of the saturated solution of the components present.[169]

At temperatures between 800° and 900°, the reaction:-

$$Cl_2 + 2KBr \rightleftharpoons 2KCl + Br_2$$

appears to involve the double anions Cl_2^{--} and Br_2^{--}; at higher temperatures (1250°) the double anions are decomposed into single ions. In the same investigation, the reaction:-

$$Cl_2 + PbBr_2 \rightleftharpoons PbCl_2 + Br_2$$

is considered to proceed through the anions Cl_4^{4-} and Br_4^{4-}.[170]

The heterogenous equilibrium:-

$$KCl(l) + HBr(g) \rightleftharpoons KBr(l) + HCl(g)$$

has been studied at 765°, and at 850°, at which temperatures the salts are fused. The equilibrium constant, K, = $N_{KBr}{\cdot}p_{HCl}/N_{KCl}{\cdot}p_{HBr}$, where N is the mole-fraction of the alkali halide, and p the partial pressure of the hydrogen halide, has the values:-

$$K_{765°} = 8{\cdot}33,\ K_{850°} = 6{\cdot}10.$$

The solid phase is a solid solution, and the heat of reaction is $-8{\cdot}5$kg.-cal./mole.[171]

The equilibrium constant for the reaction:-

$$Cl_2 + 2KBr \rightleftharpoons 2KCl + Br_2$$

has the value 303 at 800°C.[172]

The corrosion of lead in solutions of potassium bromide at 20° has been studied; the concentration of the solution was varied between 10^{-4}N, and 2N. The rate of corrosion increased with increase in concentration, and an adherent white film was formed; it is concluded that anodic adsorption of negatively charged lead bromide particles occurs.[173]

The equilibrium between sodium and fused potassium bromide, at 800°, has been studied; the mean value for the equilibrium constant, $\frac{[Na][KBr]}{[K][NaBr]}$ is $28{\cdot}8 \pm 5{\cdot}7$.[174]

The equilibrium distribution of sodium and potassium between their mixed amalgam and a solution of mixed sodium and potassium bromides has been investigated.[175] The equilibrium constant, defined by:-

$$\frac{[K/Hg]\,[NaBr]}{[Na/Hg]\,[KBr]} = K$$

varies as follows:-

i). At fixed total salt concentration, K decreases with increase of amalgam concentration.
ii). At fixed concentration of amalgam, and fixed total salt concentration, K is independent of "salt ratio".
iii). At fixed amalgam concentration, K decreases with increase in concentration of the mixed salt solution.

The irreversible reciprocal system of lithium and potassium bromides and hydroxides has been investigated. Among the nine fields of crystallization the following compounds were found:-[176]

KOH,KBr, 2LiOH,LiBr, and 2LiOH,KOH

The melting point-composition diagram for the ternary system potassium chloride-potassium bromide-potassium iodide is shown in Fig. 11.[177] The binary eutectics are:-

KBr-KCl, 734°, 71% KBr
KBr-KI, 664°, 29% KBr
KCl-KI, 588°, 47% KCl

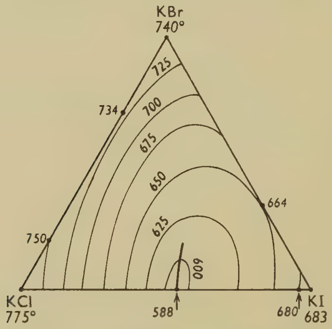


FIG. 11. THE TERNARY SYSTEM KBr-KCl-KI
734° --- 71% KBr 664° --- 71% KI 588° --- 53% KI

The melting point-composition diagram for the reciprocal salt pair sodium iodide-potassium bromide is given in Fig. 12.[178] The binary eutectics, in this case, are:-

NaBr-KBr, 635°, 48% KBr
KBr-KI, 662°, 27% KBr
NaI-KI, 580°, 58% NaI
NaBr-NaI, 650°, 72% NaI

The system potassium bromide-potassium chloride shows an unbroken series of solid solutions.[179]

The reciprocal system potassium bromide-silver chloride shows a eutectic, with melting point 320°C., at 25·1 mol.-% KBr.[180]

The system of silver bromide with mixed crystals of potassium bromide and chloride having the composition 50 mol.-% KBr/:50 mol.-% KCl, shows a eutectic at 302°C., containing 74·8 mol.-% AgBr, 25·2 mol.-% mixed crystal (i.e. 12·6 mol.-% KBr, 12·6 mol.-% KCl).[180]

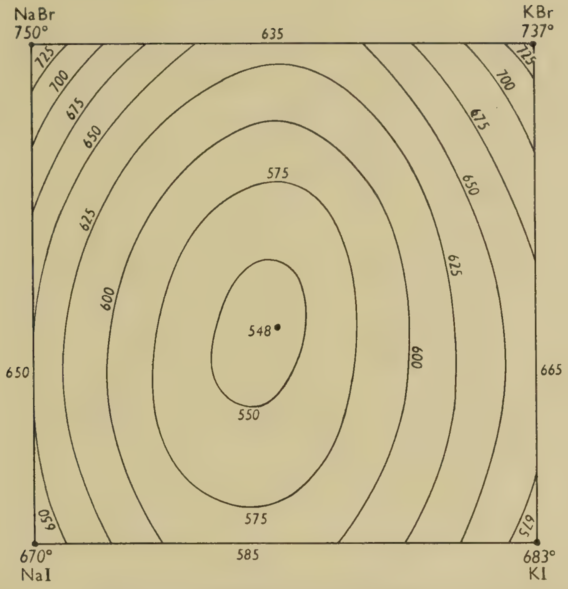


FIG. 12. THE QUATERNARY SYSTEM NaBr-KBr-KI-NaI

The validity of rules suggested for plotting phase diagrams of binary systems is demonstrated by considering the melting point–composition curves for a number of systems.[181] Table LXIX gives the results for the system potassium bromide–rubidium bromide.

TABLE LXIX.- MELTING POINT, AND COMPOSITION, OF THE SYSTEM POTASSIUM BROMIDE–RUBIDIUM BROMIDE[181]

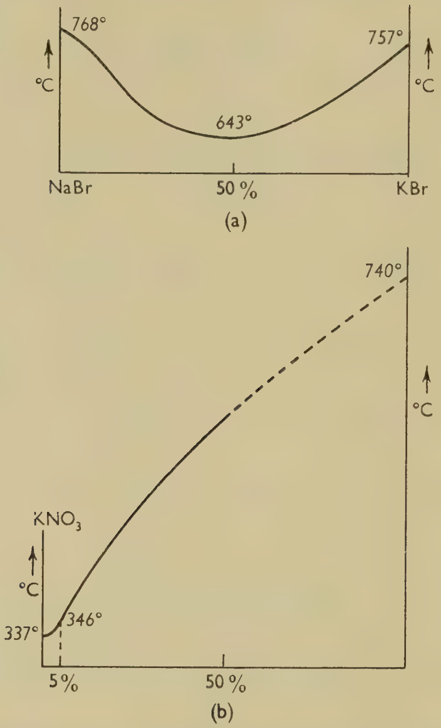
Mol.-% KBr	m.p.	Mol.-% KBr	m.p.
0	680	50	685
10	675	60	691
20	668	70	700
25	670	80	708
30	673	90	719
40	678	100	730

The reciprocal system of potassium and sodium bromides and hydroxides shows six fields of crystallization. Four of these were of the pure components, and the remainder of the compounds KOH,KBr, and NaOH,NaBr.[182]

Potassium and sodium bromides and nitrates form a typical reversible reciprocal system. The crystallization area is divisible into three fields: continuous solid solutions of potassium and sodium bromides occupy 91% of the area, continuous solid solutions of potassium and sodium nitrates a further 8%, a field of KNO_3,KBr occupying the remaining 1%. Melting point–composition diagrams, for the binary systems present, are shown in Figs. 13 and 14.[183]

The systems potassium bromide–potassium chloride–water, and potassium bromide–rubidium bromide–water, both show at 25° formation of type-II solid solutions, by the Roozeboom classification. The compositions of the liquid and solid solution phases, in equilibrium, are recorded in Tables LXX and LXXI.[184]

The equilibria of aqueous solutions containing bromine and potassium compounds have been studied in connection with the problem of commercial recovery of bromine from natural sylvites and carnallites.



(a)

(b)

FIGS. 13a, 13b. MELTING POINT-COMPOSITION DIAGRAMS FOR THE BINARY SYSTEMS NaBr-KBr AND KNO$_3$-KBr

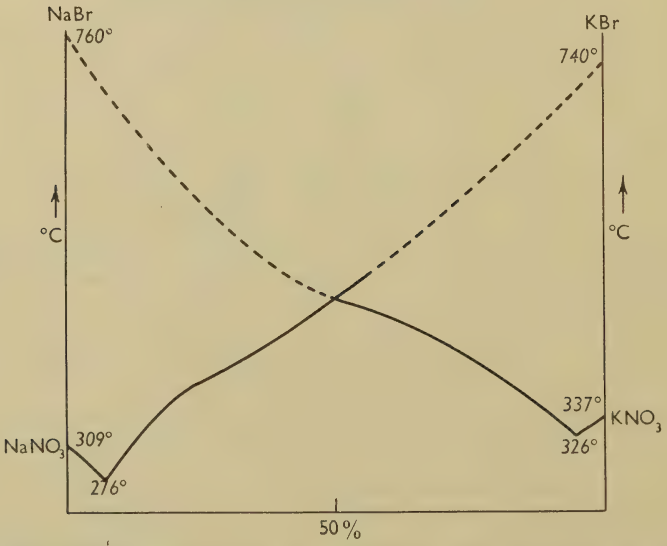


FIG. 14. MELTING POINT-COMPOSITION DIAGRAMS FOR THE BINARY SYSTEMS NaBr-KNO$_3$ and KBr-NaNO$_3$

The data for the systems potassium bromide-potassium chloride-water, and potassium bromide–magnesium bromide–water, are recorded in Tables LXXII and LXXIII.[185]

TABLE LXX.- EQUILIBRIUM DATA FOR THE SYSTEM POTASSIUM BROMIDE (A)–POTASSIUM CHLORIDE (B)–WATER, AT 25°C.

Overall Composition		Liquid		Solid Soln.	
Wt.-% A.	Wt.-% B.	Wt.-% A.	Wt.-% B.	Wt.-% A.	Wt.-% B.
0	–	0	26·4	0	100
10	25	10·2	20·8	–	–
21	22	20·2	15·4	27·0	73·0
25	21	22·8	13·9	37·6	62·4
34	18	26·5	11·6	60·0	40·0
37	10	30·5	8·72	81·1	18·9
39	5	35·1	4·82	92·9	7·1
–	0	4·06	0	100	0

TABLE LXXI.- EQUILIBRIUM DATA FOR THE SYSTEM POTASSIUM BROMIDE (A)–RUBIDIUM BROMIDE (B)–WATER, AT 25°C.

Overall Composition		Liquid		Solid Soln.	
Wt.-% A.	Wt.-% B.	Wt.-% A.	Wt.-% B.	Wt.-% A.	Wt.-% B.
0	–	0	52·23	0	100
6·9	51·1	6·96	45·4	6·4	93·6
11·2	45·8	10·86	41·1	14·5	85·5
16·5	39·7	15·3	36·0	26·5	73·5
21·43	33·64	19·35	30·95	41·1	58·9
29·04	23·92	25·28	23·1	66·3	33·7
38·17	12·95	32·11	12·88	86·7	13·3
–	0	40·65	0	100	0

TABLE LXXII.- EQUILIBRIUM DATA FOR THE SYSTEM POTASSIUM BROMIDE–POTASSIUM CHLORIDE–WATER, AT 25°C.

Overall Composition			Solid Phase		
% KCl	% KBr	% Water	% KCl	% KBr	% Water
25·88	1·80	72·32	98·10	1·30	0·60
17·90	15·5	66·60	85·37	14·30	0·33
14·28	22·22	63·50	48·7	50·5	0·60
9·78	29·25	60·97	23·14	75·48	1·38
8·02	31·45	60·53	11·88	87·23	0·90
2·08	37·51	60·41	4·50	94·10	1·40

The solid phase consists of a complete range of solid solutions.

TABLE LXXIII.- EQUILIBRIUM DATA FOR THE SYSTEM POTASSIUM BROMIDE–MAGNESIUM BROMIDE–WATER, AT 25°C.

Overall Composition			Solid Phase
% KBr	% $MgBr_2$	% Water	
40·81	0	59·19	KBr
35·29	4·77	59·94	KBr
30·23	9·23	60·54	KBr
18·14	20·67	61·19	KBr

continued on following page

TABLE LXXIII.- CONTINUED.

Overall Composition			Solid Phase
% KBr	% $MgBr_2$	% Water	
12·01	28·01	59·98	KBr
6·13	36·35	57·52	KBr
5·17	37·86	56·97	KBr
2·68	43·24	54·08	KBr + $KBr,MgBr_2,6H_2O$
0·91	48·23	50·86	(50·53% KBr, 31·65% $MgBr_2$, 17·82% Water)
0·14	50·43	49·43	$KBr,MgBr_2,6H_2O$ + $MgBr_2,6H_2O$
0	50·60	49·40	$MgBr_2,6H_2O$

Potassium bromide shows a homeomorphic transformation at 22°. The system potassium bromide–potassium chloride–water is simple, only two crystalline fields being observed: ice, and solid solutions of potassium bromide and chloride.[186] The solid solution field was divided into α– and β– homeomorphs.

In the system potassium bromide–sodium bromide–water, the components crystallize in their pure states. The six crystal fields meet in four ternary points, and the eutectic at –32° has the composition 91·34 NaBr, 8·66 KBr, 850 H_2O, moles. At this point, the fields of $NaBr,5H_2O$, KBr, and ice meet.[186]

Isothermal evaporation studies have been carried out on the systems potassium bromide–potassium chloride–water, and potassium and sodium bromides–potassium and sodium chlorides–water.[187]

The reciprocal system potassium and sodium bromides–potassium and sodium carbonates shows two fields of solid solutions, with a ternary eutectic at 575°, of composition Na_2CO_3 32, K_2Br_2 32, Na_2Br_2 36, mol.-%. The phase diagram is shown in Fig. 15. For the exchange reaction:-

$$Na_2Br_2 + K_2CO_3 \rightleftharpoons K_2Br_2 + Na_2CO_3$$

ΔH = 1·8 kg.-cal./equivalent, so that equilibrium is shifted to the KBr–Na_2CO_3 salt pair.[188]

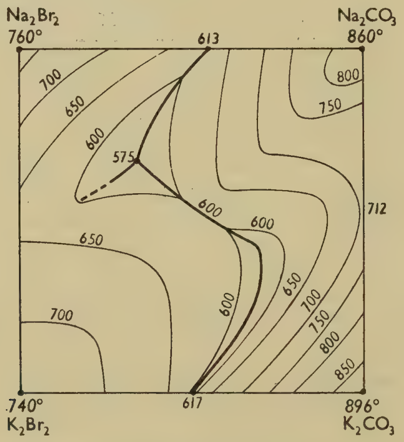


FIG. 15. THE QUATERNARY SYSTEM, Na_2Br_2-Na_2CO_3-K_2CO_3-K_2Br_2

Solubility, viscosity, and specific gravity studies have been made on the ternary system potassium bromide–potassium iodide–water, at 0°, 15°, 35°, and 50°.[189] The system shows two limited fields of solid solutions which meet at a point; here the viscosity and specific gravity isotherms break sharply.

Similar behaviour is shown by the system KBr–NaBr–H_2O.[189a]

Equilibria in the system potassium bromide–potassium bromate–water, have been studied, at temperatures from 0° to 80°.[190] The mutual solubility curves for this system are shown in Fig. 16.

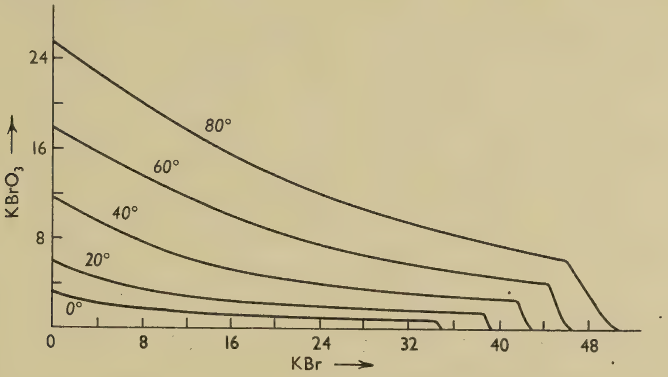


FIG. 16. MUTUAL SOLUBILITY CURVES OF KBr AND $KBrO_3$

The ternary system potassium bromide–potassium iodate–water has been investigated, with the results listed in Table LXXIV.[191]

TABLE LXXIV.- EQUILIBRIA IN THE SYSTEM POTASSIUM BROMIDE–POTASSIUM IODATE–WATER, AT 25°C.

Original Wt.-%		Solid Soln. Wt.-%		Density	Solid Phase
KBr	KIO_3	KBr	KIO_3		
–	0	40·62	0	1·381	KBr
50·57	0·81	40·28	0·98	1·396	KBr
46·94	3·09	39·75	2·36	1·407	KBr + KIO_3
41·03	9·04	39·75	2·36	1·408	KBr + KIO_3
34·99	15·98	39·75	2·36	1·407	KBr + KIO_3
29·97	15·07	34·38	2·47	1·341	KIO_3
22·52	15·53	25·91	2·73	1·249	KIO_3
15·02	16·50	17·40	3·26	1·168	KIO_3
0	–	0	8·452	1·071	KIO_3

No double salt formation is indicated, either at 25°C. or at 5° and 50°C.

The ternary system potassium bromide–potassium chloride–50% ethanol has been studied at 35°C.[192] The data are recorded in Table LXXV.

TABLE LXXV.- EQUILIBRIA IN THE SYSTEM POTASSIUM BROMIDE–POTASSIUM CHLORIDE–50% ETHANOL, AT 35°C.

Original Wt.-%		Solution, Wt.-%		Density	Solid Soln.
KCl	KBr	KCl	KBr		Wt.-% KBr
–	100	–	17·21	–	100
0·99	27·13	0·75	16·28	1·016	99·01
1·46	26·72	1·02	15·96	1·006	95·70
2·28	25·92	1·51	15·34	1·004	92·82
2·99	25·16	1·76	15·00	1·001	89·25
4·02	23·06	2·27	14·22	0·998	83·91
5·03	21·08	2·06	13·81	1·001	76·22

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TABLE LXXV.- CONTINUED.

Original Wt.-%		Solution, Wt.-%		Density	Solid Soln.
KCl	KBr	KCl	KBr		Wt.-% KBr
6·02	19·09	3·00	12·95	0·995	69·27
7·03	18·05	3·18	12·65	0·990	61·61
8·04	17·09	3·50	11·91	0·993	57·01
9·03	15·11	3·80	11·27	0·983	47·19
10·08	13·08	4·11	10·35	0·978	37·17
12·07	10·09	4·70	8·47	0·971	24·13
14·06	6·05	5·64	5·45	0·958	11·30
16·23	2·14	6·09	2·09	0·938	2·54
100	—	7·31	—	—	0

The system belongs to type II of the Roozeboom classification, as for the same salts with water as solvent; change of solvent causes a shift of the crystallization end point, from 65·5 to 83·5 mol.-% KBr.

The "salt temperature" has been determined, for saturated solutions of various pairs of salts. When a solution containing two salts is boiled, it becomes more concentrated and the boiling point rises; the maximum, in the presence of a small quantity of separated salt, is termed the "salt temperature".[193] For the pair potassium bromide–potassium chloride, the salt temperature is 111·3°, and the solid composition is 17% KCl, 83% KBr; the boiling points of saturated solutions of the component salts are 110·9° (KBr) and 108·5° (KCl).

The reciprocal system potassium bromide–rubidium chloride has been studied, and the results of *X*-ray diffraction analysis are compared with refractivities. Refractive index–composition, and melting point–composition, curves are shown in Figs. 17 and 18.[194] All observations accord with the view that one solid solution is formed which contains all the ions for each mixture.

In a study of reactions between dry inorganic salts, the unstable pair sodium bromide-potassium chloride were observed to change partially towards sodium chloride-potassium bromide at 25° and under 3500 atm.[195]

The system potassium bromide–bromine–water was studied at low concentrations of bromide and at 0°. A bromine hydrate, $Br_2 10H_2O$, was the only hydrate observed.[196]

A study of this system by the wet-residues method, at 0°, indicated the existence of solid compounds with incongruent melting points: $Br_2,7H_2O$ (5·85°), and $KBr_6,1{\cdot}5H_2O$(25·85°). The latter is a diamagnetic solid, in equilibrium at its melting point with a solution containing by weight 21·4% KBr, 70·4% Br_2, and 8·2% water.[197]

From cryoscopic studies, the mean equilibrium constant for the formation of potassium tribromide, KBr_3, is 22·87, at a mean temperature of −0·65°. For the salt $KClBr_2$, $K_{mean} = 5{\cdot}739$, $t_{mean} = -0{\cdot}98°$.[198]

The solubilities of bromine and iodine in solutions of alkali halides were determined at 30°, in an investigation of polyhalides.[199] The data for potassium bromide solutions are listed in Table LXXVI.

Solubilities are measured in g. per 25ml. of potassium bromide solution saturated with the halogen.

No equilibrium constant was obtained from the bromine solubilities, and it was concluded that KBr_3 does not exist at 30°.

The distribution of bromine between water and potassium bromide solutions gives the value for the equilibrium constant of $Br_2 + Br^- \rightleftharpoons Br_3^-$ as 16·0 at 25℃. From the solubility of the bromine in potassium bromide solutions, of concentration 0·01 to 1·0 molar, the equilibrium constant for $2Br_2 + Br^- \rightleftharpoons Br_5^-$ at 25℃. is 40.[200]

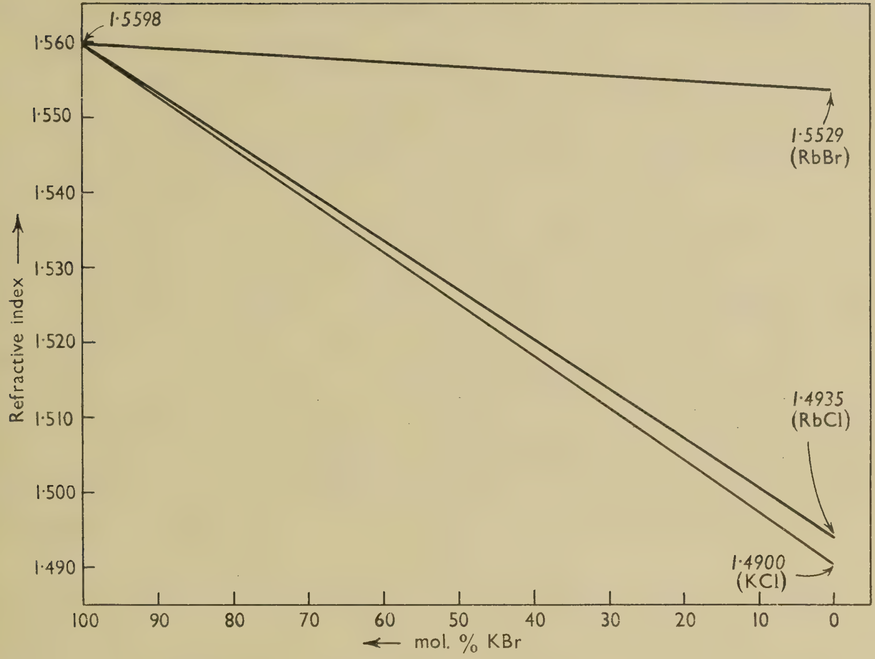

FIG. 17. REFRACTIVE INDEX-COMPOSITION DIAGRAMS FOR THE BINARY SYSTEMS KBr-RbBr, KBr-RbCl, KBr-KCl

TABLE LXXVI.- SOLUBILITIES OF BROMINE AND IODINE IN AQUEOUS SOLUTIONS OF POTASSIUM BROMIDE, AT 30 °C.

N_{KBr}	Soly. Br	Soly. I	$K_{30°C.}$ $KBrI_2$
4	–	0·3603	16·97
3	6·013	0·2813	14·94
2	4·117	0·1966	13·25
1	2·031	0·1053	12·47
0·5	1·144	0·0595	12·43
0·25	0·7513	0·0302	12·49
0·125	0·5201	0·0238	13·06
0·0625	0·4358	0·0175	13·96
0	0·3123	0·0099	–

From the conductivities of saturated solutions of bromine in potassium bromide, it is concluded that the acid HBr_3 is only a little weaker than hydrobromic acid.[201]

From light absorption studies of solutions of potassium halides and free halogens, the existence of the compounds KBr_3, $KClBr_2$, and $KBrI_2$ is indicated. These complexes appear to be more stable in ethanol than in water; instability constants are listed in Table LXXVII.

Investigation of the system potassium bromide–bromine–water at 0° indicated the existence of a solid potassium polybromide $2KBr_6,3H_2O$; no anhydrous polybromide was indicated in the corresponding sodium bromide system, nor was any complex formed. The potassium polybromide hydrate crystallized in long red needles, melting (in a sealed tube) at 25°.[203]

The results obtained in a number of studies of this system have been summarised.[204]

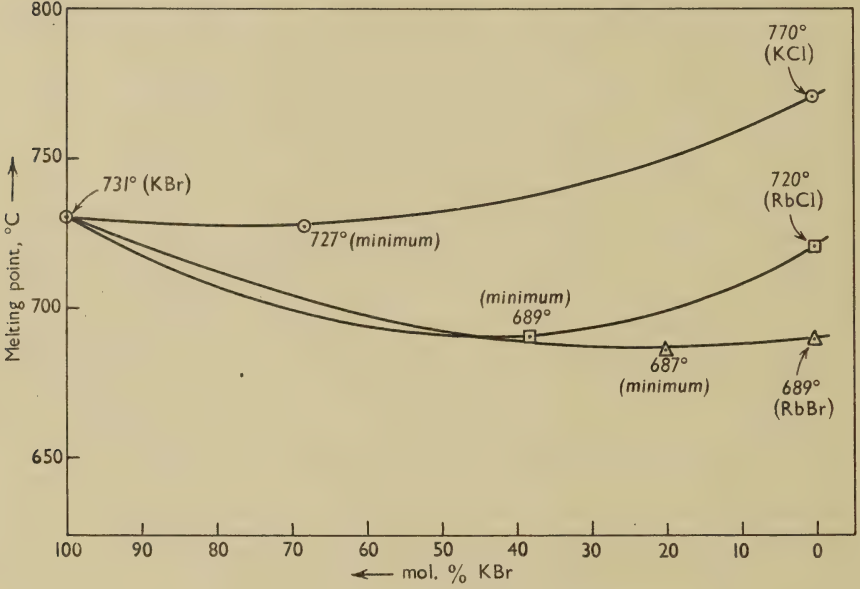

FIG. 18. MELTING POINT-COMPOSITION DIAGRAMS FOR THE BINARY SYSTEMS KBr-KCl, KBr-RbCl, KBr-RbBr

TABLE LXXVII.- INSTABILITY CONSTANTS OF COMPLEXES INVOLVING POTASSIUM BROMIDE, AT t°C., IN WATER AND ETHANOL.[202]

Complex	$K_{inst.}$ water	t°C.	$K_{inst.}$ ethanol	t°C.
KBr_3	$3 \cdot 5 \times 10^{-2}$	16	$2 \cdot 7 \times 10^{-4}$	14
	$6 \cdot 3 \times 10^{-2}$	5	—	—
$KBrI_2$	$5 \cdot 4 \times 10^{-2}$	16	$1 \cdot 0 \times 10^{-3}$	15
	$7 \cdot 8 \times 10^{-2}$	5	—	—
$KClI_2$	$2 \cdot 8 \times 10^{-1}$	16	—	—
	$4 \cdot 3 \times 10^{-1}$	5	—	—
$KClBr_2$	$1 \cdot 9 \times 10^{-1}$	16	—	—

The complex halide potassium dibromoiodide, $KIBr_2$, prepared as already described (Mellor, II, 610 - 611) was observed to crystallize from saturated aqueous solution as the monohydrate.[205] The halogen of a polyhalide may be replaced by a more electronegative one, as in:-

$$KIBr_2 + Cl_2 \rightarrow KICl_2 + Br_2$$

Oxidation of potassium dibromoiodide by ozone yields bromine and potassium iodate. The structure of this compound is:-[206]

$$K^+ (Br{-}I{-}Br)^-$$

Analysis

The titration of potassium bromide solutions with silver nitrate by Fajan's method (using an adsorption indicator) has been found to give good results in the presence of nitric or sulphuric acid, with Tropæolin OO, Sodium Alizarin Sulphonate, Bromophenol Blue, Formyl Violet, or Congo Red, as indicator.[207]

In the accurate analysis of solutions by refractometry, allowance must be made for the variation of refractive index increments; for potassium bromide solutions the increment, expressed as *n* per 1%, varies from 0·00119, at 5·31%, to 0·00113, at 20·15%.[208]

In the potentiometric titration of 0·1 N-potassium bromide with 0·1 N-silver nitrate, against the glass electrode, curves showing a characteristic maximum near the end-point were obtained. The reverse titration, of silver nitrate with potassium bromide, produces a minimum. Addition of 1% of gelatin changed the shapes of the curves; addition of electrolytes lowered the maximum and minimum.[209]

The detection of iodine as an impurity in potassium bromide may be carried out in the following way.[210] To a 5% solution of the potassium bromide is added five drops each of 0·1N-potassium permanganate and 5N-hydrochloric acid. The solution is then extracted with 2 c.c. of xylene; both bromine and iodine are liberated, the bromine reacting with the xylene, leaving the iodine to colour the immiscible layer. The limit of detection is said to be 0·0004g. of iodine.

Uses

The electrolytic preparation of potassium bromate from potassium bromide solution has been studied.[211] Carbon electrodes give higher energy efficiency than platinum; the pores must be filled with a paraffin, to prevent the otherwise rapid disintegration. The use of a depolariser, such as potassium dichromate, is essential for high yields.

For photographic use, a non-caking potassium bromide is required. Small amounts of B_2O_3 (0·05%), HBO_2 (0·5%) or H_3BO_3 (0·5%) prevent caking, but do not interfere with the developing process.[212]

A mixture of potassium bromate and potassium bromide, in the ratio of 10:1 is suggested for use as a herbicide; metal chlorides and iron salts may be incorporated as catalysts.[213]

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SECTION LIII

POTASSIUM IODIDE

By W. H. LEE and M. F. C. LADD

Preparation

Potassium iodide may be obtained by treating an aqueous solution of potassium hydroxide, carbonate, or bicarbonate with iodine, and reducing the oxyhalogen compound with various iron–carbon galvanic couples.[1]

The preparation of ferroso-ferric iodide, from the stoicheiometric proportions of iron and iodine, has been described; decomposition with potassium carbonate, at 70°–80°, yields potassium iodide.[2-4] Aluminium may replace iron in this process; at the optimum concentrations of 0·8 molar aluminium iodide (Al_2I_6) solution and molar potassium carbonate, the yield of potassium iodide is nearly 99%.[5]

From technical-grade potassium chloride, pure potassium iodide, in a 96% yield, was obtained by distillation with constant-boiling hydriodic acid; all the hydrogen chloride was removed, with a very small amount of hydrogen iodide. The pure crystalline salt separated in the distillation flask, and was washed and dried. Technical-grade potassium bromide may replace the chloride.[6]

Potassium iodide free from solid by-products may be obtained by reducing a solution of iodine in potassium hydroxide with formic acid or formaldehyde using specified concentrations and temperatures.[7]

Potassium iodide may be purified in solution by the following procedure. A solution of a barium halide is added, to remove sulphate, and any iron present is oxidized by hydrogen peroxide. Alkaline-earth metals are precipitated by addition of a metal carbonate. The pH is reduced to 6·5, and on boiling aluminium, magnesium and silicon are removed. Carbon dioxide is boiled off, and the purified salt crystallized out.[8]

Large crystals of potassium iodide, suitable for infra-red dispersion, have been grown by slowly racking up a water-cooled spindle from the melt.[9]

Controlled evaporation of potassium iodide solutions on a microscope slide has enabled the effect of evaporation rate on the faces developed to be studied.[10] Critical rates were observed, above which only octahedra are produced; these rates have been studied in aqueous, and in non-aqueous, solutions.[11] The degree of supersaturation of the solution has also been found to affect crystal form.[12] The addition of sodium nitrate (5·07A.) to potassium iodide solution produced octahedra of potassium iodide (4·97A.) but not of sodium chloride (3·07A.); these figures in parentheses are the interionic distances in the (111) plane, all the ions in one plane being alternately metal and halogen.[13]

Physical Properties

Precise determinations of the lattice constant of potassium iodide, by electron and X-ray diffraction, show excellent agreement: $a = 7{\cdot}051$A., within the experimental error of the former technique of ±0·05%. For crystallites of less than 100A. side, the lattice constant was about 0·5% less.[14]

The following values are quoted, in the A.S.T.M. *X*-ray Index, for the lattice constant and density of potassium iodide, at 25°: a = 7·0655A., d = 3·1257.[15] A later value, for spectrographically standardized material, at 25°, is: $a = 7{\cdot}0655(5) \pm 0{\cdot}00001(5)$A.[16]

For mixed crystals of potassium iodide and potassium bromide, additivity of lattice constant, a_{12}, is observed over a limited range of compositions: $a_{12} = a_1x + a_2(1 - x)$, where a_1 is the lattice constant of the component of weight-fraction x.[17]

The lattice energy of potassium iodide has been recalculated, with the results recorded in Table I.

TABLE I.- LATTICE ENERGY OF POTASSIUM IODIDE

U (kg.-cal./mole)	166	149	151	150·6	152	152	149
Ref.	18	19	20	21	22	23	23
Method	a	b	c	d	e	f	g

a: Born–Haber cycle, taking the electron affinity of iodine as −59·2 kg.-cal./g.-atom; cf. the later value of −72·6 kg.-cal.[24]
b: Born–Haber cycle, taking the electron affinity of ref. 24.
c: thermodynamic equation based on the elastic properties of the crystal.
d: study of the dissociation equilibrium of potassium iodide vapour at high temperatures.
e: calculation assuming basic radii.
f: modified Born–Haber cycle.
g: electrostatic model, allowing for dipole–dipole and dipole–quadrupole interactions.

The surface energy, defined as the work per square centimetre required to split the large crystal along a particular face and remove one half to infinity, has been calculated. The surface energy of the (001) face, for potassium iodide, is 74·9 kg.-cal./mole, and that of the (011) face 203·0 kg.-cal./mole.[25]

The orientation of overgrowths of potassium iodide on sodium chloride as substrate have been studied.[26] The grown or deformed metals and alloys have in general fibre-like structures; this has also been observed for potassium iodide, amongst other alkali-halide crystals, grown from the melt.[27] On mica, overgrowths of potassium iodide are oriented to the larger atomic network of the substrate.[28] No orientation of potassium iodide overgrowths was observed on potassium chloride substrate,[29] but orientation upon sodium chloride was confirmed. In a later study, however, evaporation in a vacuum on to cleavage surfaces of lithium fluoride, sodium chloride, potassium chloride and potassium bromide, produced oriented overgrowths of potassium iodide. The crystallographic axes of the deposit were parallel to those of the substrate.[30] Electron diffraction shows that thin deposits of potassium iodide on cleavage faces of calcium carbonate or sodium nitrate are arranged regularly; but the orientation is random for thicknesses above 150A.[31] Orientation of overgrowths of potassium iodide on silver as substrate was observed, for deposition from both the vapour phase and from solution.[32]

Thin layers (about 10A. in thickness) of potassium iodide, deposited on a potassium iodide substrate, consisted of a part with the same orientation as the substrate, and a part in the twin position (111) to it.[33]

The heat of formation of mixed crystals has been calculated from the equation:-

$$\Delta H_f = U_0/b.(1 + \gamma_n x)^{1/n} - xU_0/a - (1 - x)U_0/b$$

where a and b are the lattice constants of the pure components, x is the mole-fraction of the component of lattice constant a, n is an integer, U_0 is the 'electrostatic' lattice energy, and $\gamma_n = a^n/b^n - 1$. The values obtained are

TABLE II. - CALCULATED AND EXPERIMENTAL HEATS OF FORMATION OF MIXED-CRYSTALS FOR POTASSIUM IODIDE–POTASSIUM CHLORIDE AND POTASSIUM IODIDE–POTASSIUM BROMIDE

KCl–KI			
Mol.-% KCl	ΔH_f expt.	ΔH_f calc.	n
0·1	−0·44	−0·40	3
0·5	−0·6	−0·55	1
0·9	−0·34	−0·35	2
KBr–KI			
Mol.-% KBr	ΔH_f expt.	ΔH_f calc.	n
0·25	−0·5	−0·41	4
0·50	−0·63	−0·81	8
0·75	−0·5	−0·58	8

given in Table II.[34] The value of the repulsion exponent n giving best agreement between experimental and calculated heats of formation is recorded; some of the values appear very small when compared with those applicable to pure components.

It has been shown by X-ray analysis that the same solid solution is obtained, in the system potassium bromide–potassium iodide, whether the solid is grown from a saturated solution or from a melt with the same ratio of these components.[35]

The refractive indices of large crystals of potassium iodide, at wavelengths from 14–29 microns (μ), have been measured; for a crystal of facial area 5·8 × 8·5 cm.^{2}, the results recorded in Table III were obtained.[36]

TABLE III. - REFRACTIVE INDICES OF POTASSIUM IODIDE AT 38°, FROM $\lambda = 14$ TO 29μ

$n_{38°}$	λ,μ	$n_{38°}$	λ,μ
1·6128	14	1·5895	22
1·6107	15	1·5858	23
1·6082	16	1·5819	24
1·6056	17	1·5775	25
1·6027	18	1·5729	26
1·5997	19	1·5681	27
1·5964	20	1·5629	28
1·5930	21	1·5571	29

A discrepancy has been reported between thermal expansion coefficients of potassium iodide as measured by X-ray methods and by macro methods.[37] The results obtained are as follows:-

Over the temperature range 20°–100°, $10^6\alpha$ = 40·6, 40·8.
Over the temperature range 20°–190°, $10^6\alpha$ = 42·1, 42·7.

The first figure in each case is the more recent X-ray result.[37a]

If the coulombic part of the lattice energy of potassium iodide is taken to be 163 kg.-cal./mole, and the repulsion exponent is 12·3, the coefficient of linear expansion is calculated to be 53·1 × 10^{-6}. The experimental value is 40·7 × 10^{-6}.[38]

The specific gravity and the volume expansion of potassium iodide have been measured at a number of temperatures, with the results recorded in

TABLE IV. - SPECIFIC GRAVITY OF POTASSIUM IODIDE

Temperature, °C.	Specific gravity	Reference
−184	3·196(8)	39
−79	3·157(7)	39
	3·161(3)	39
0	3·132(5)	Mellor, II, 599
	3·124(9)	Mellor, II, 599
21	3·118(0)	39

TABLE V. - VOLUME EXPANSION OF POTASSIUM IODIDE

Temp. range °C.	10^4(vol. expansion coeff.)	Reference
−184 to −79	1·16	39
−79 to 0	1·25	39
0 to 50	1·17	Mellor, II, 603

Tables IV and V.

The compressibility of potassium iodide and its variation with pressure and temperature have been measured. The results are as follows (κ = compressibility):-[40]

$10^{12}\kappa_{30^\circ}$	$10^{12}\kappa_{273^\circ}$	$10^{12}(\delta\kappa/\delta P)_T$	$10^4(\delta\kappa/\delta T)_P$
$8{\cdot}54 \pm 0{\cdot}009$	$7{\cdot}0 \pm 0{\cdot}007$	$39{\cdot}1 \pm 2{\cdot}0$	$6{\cdot}0 \pm 1{\cdot}2$

This value of $(\delta\kappa/\delta P)_T$ applies at pressures up to 12,000 atm., and over the temperature range 30°–75°. $(\delta\kappa/\delta T)_P$ applies within the temperature range 30°–75°.

The elastic moduli of potassium iodide have been measured: $C_{11} = 3{\cdot}32 \times 10^{11}$, $C_{12} = 0{\cdot}578 \times 10^{11}$, $C_{44} = 0{\cdot}620 \times 10^{11}$. The value of Young's modulus is $3{\cdot}15 \times 10^{11}$, and of the modulus of rigidity, $0{\cdot}620 \times 10^{11}$.

The melting point of potassium iodide by direct observation is 723°C.[42] The boiling point and the critical temperature were found to be 1319°C. and 2195°C., respectively.[43] It is considered that a more reliable value for the boiling point is 1420°C.[42] The molar heat of vaporization is 38·1 kg.-cal./mole.[43]

The vapour pressure of potassium iodide, at various temperatures, has been measured; the results may be represented by the formula: $\log p(\text{atm.}) = -(37{,}150/4{\cdot}57T) + 5{\cdot}0685$. The experimental results are given in Table VI,[44] together with those calculated from the formula.

TABLE VI. - VAPOUR PRESSURE OF POTASSIUM IODIDE (t in °C.)

p mm.	t(exp.)	t(calc.)	δt
69·5	1063	1059	+4
147·2	1130	1133	−3
150·2	1134	1136	−2
271·8	1202	1201	−1
531·1	1285	1283	+2
540·9	1285	1286	−1
763·2	1333	1333	0

From the deflection of molecules of potassium iodide in an inhomogeneous electric field, the value 10^{-17}c.g.s. units was obtained for the electric moment.[45] From a similar investigation, the dipole moment at 941° was found to be 6·8D.[46]

When molecular beams of potassium iodide are ionized by 0–150-volt electrons, the following ions are observed:[47] K_2I^+ (7•1), KI^+ (8•3), K^+ (8•1), I^+ (14•4). The values in parentheses are the ionization potentials; the relative current intensities due to these ions are 1•2, 22•5, 58•8 and 17•5, respectively (% current at 60V.). It is concluded that alkali metal halides evaporate in such forms as M_2X_2 and M_2X, as well as in the simple form MX.

In mass-spectrometric analysis of potassium iodide vapour, the intensity of K^- was only 1/25 of that of I^-.[48]

The specific heat of potassium iodide within the temperature range 20° to 660° is expressed by:-

$$\bar{c}_p = 0{\cdot}0728 + (1{\cdot}69 \times 10^{-5})t,$$

the mean deviation being 0•1%. The true specific heat c_p is given by:-

$$c_p = d/dt\{\bar{c}_p(t - 20)\} \text{ g.-cal./g.},$$

described by:-

$$c_p = 0{\cdot}0725 + (3{\cdot}4 \times 10^{-5})t.$$

The molar heat capacity, C_p, is $12{\cdot}04 + (5{\cdot}60 \times 10^{-3})t$ g.-cal.[49] The enthalpy and molar heat capacity of potassium iodide have been measured at temperatures within the range 300° to 700° with the results shown in Table VII.[50]

TABLE VII. - ENTHALPY AND MOLAR HEAT CAPACITY OF POTASSIUM IODIDE

t° C.	H, kg.-cal./mole	C_p, g.-cal.
300	3•94	13•15
350	4•60	13•54
400	5•29	13•88
450	6•00	14•19
500	6•72	14•40
550	7•46	14•56
600	8•20	14•68
650	8•94	14•79
700	9•68	14•87

The molar entropy of potassium iodide is 24•94 g.-cal./mole/°C., at 298•16°K.[51] The heat of formation, $\Delta H_f°$, is −79•67 kg.-cal./mole, and the free energy of formation, $\Delta G_f°$, is −77•52 kg.-cal./mole, both at 298•16°K.[52,53]

The heats of formation of solid solutions of potassium iodide and rubidium iodide have been calculated, and are recorded in Table VIII.[54]

TABLE VIII. - HEATS OF FORMATION OF MIXED CRYSTALS OF POTASSIUM IODIDE AND RUBIDIUM IODIDE

Mol. fraction KI	ΔH_f
0•17	88 g.-cal./mole
0•34	136 g.-cal./mole
0•50	151 g.-cal./mole
0•66	139 g.-cal./mole
0•83	93 g.-cal./mole

These theoretical heats of formation apply to equilibrium at 50°C., and are closely proportional to the expression $(\delta R)^2/R_0^3$; where δR is the difference between the interionic equilibrium distances in the pure components and R_0 the interionic distance in the solid solution.[55]

The decomposition potential (E_v) of potassium iodide has been determined over the temperature range 700° to 1000°, as recorded in Table IX.[56]

TABLE IX. - DECOMPOSITION POTENTIALS OF POTASSIUM IODIDE, AT VARIOUS TEMPERATURES

t°C.	E_v, V.
706	2•660
741	2•610
773	2•564
783	2•561
804	2•520
822	2•502
885	2•412
916	2•364
946	2•322
972	2•278
1024	2•198

At temperatures between 690° and 814°, it is found that the molar electrical conductivity, μ_t, of potassium iodide follows the relationship:-[57]

$$\mu_t = 85{\cdot}41 + 0{\cdot}1564(t - 700)$$

The vapour pressures of mixtures of potassium iodide with sodium iodide and with potassium chloride have been measured at 1180°; the results are as follows:-[57a]

KI–NaI

Mol.-% KI	0	25	50	75	100
p_{KI}, mm.	-	60•3	115•1	177•6	231
p_{KCl}, mm.	260	189•1	132•9	66•8	-

KI–KCl

Mol.-% KI	0	25	50	75	100
p_{KI}, mm.	-	54•5	117•2	172•3	231
p_{KCl}, mm.	106	80•8	57•1	23•6	-

The electrical conductivities and densities have been measured for the molten salt mixtures potassium iodide–sodium chloride, and potassium iodide-cadmium iodide. In Table X, the constants A_K and E_K in the conductivity expression, $\kappa = A_K \exp(-E_K/RT)$, and a and b in the density relationship, $\rho = a - bt$, are listed.[58]

From measurements of electrical conductivity and density of molten potassium iodide, the equivalent conductance Λ is found to vary with temperature, within the range 685° to 911°,[60] according to the relationship:-

$$\log\Lambda = 3{\cdot}91176 - \frac{1932{\cdot}37}{T} + 2{\cdot}53113 \log(10^3/T).$$

The experimental values of specific conductance κ are recorded in Table XI.

The electrical conductivity and density have also been measured for the molten-salt system potassium iodide–potassium chloride.[60] The specific conductance is given as a function of temperature by $\kappa = -a + bt - ct^2$. The coefficients a, b and c, applicable at various compositions, are listed in Table XII. The standard deviation in κ is less than 0•003.

The densities of mixtures within this system may be expressed by: $\rho = a' - b't$; values of the coefficients a' and b' for various compositions are listed in Table XIII. The standard deviation of ρ is less than 0•0005.

TABLE X.- CONSTANTS IN THE ELECTRICAL CONDUCTIVITY AND DENSITY EQUATIONS FOR MOLTEN-SALT MIXTURES

Mol.-% KI	A_K	E_K, kg.-cal./mole	a	$10^4 b$	Upper t° limit
Potassium Iodide–Sodium Chloride					
100	5•81	2•85	3•108	9•60	800
85	7•83	3•21	3•034	9•65	800
70	8•94	3•28	2•893	8•58	800
50	9•62	3•15	2•727	8•19	800
30	11•0	3•07	2•484	7•06	800
15	13•2	3•11	2•253	6•32	800
0	7•45*	1•58*	2•010	5•66	800
Potassium Iodide–Cadmium Iodide					
100	5•81	2•85	3•108	9•60	800
95	7•81	3•53	–	–	800
90	8•58	3•80	–	–	800
85	–	–	3•469	10•92	800
80	7•00	3•60	–	–	800
75	38•5	6•38	–	–	800
66•6	8•02	3•80	3•769	11•15	800
55	6•64	3•53	–	–	800
50	–	–	4•120	12•22	700
47•5	7•26	3•56	–	–	700
42	5•10	3•18	–	–	700
33•3	–	–	4•431	12•91	700
20	5•19	3•39	–	–	700
15	–	–	4•645	11•70	700
0	25•3	6•34	4•828	11•17	700

* Results of previous investigation.[59]

TABLE XI.- SPECIFIC CONDUCTANCE OF FUSED POTASSIUM IODIDE, AT VARIOUS TEMPERATURES

t°, C.	κ_t	t°, C.	κ_t	t°, C.	κ_t
685•4	1•244	739•5	1•413	791•1	1•502
689•0	1•261	745•7	1•421	815•7	1•544
697•5	1•294	754•3	1•440	830•7	1•564
698•5	1•296	768•2	1•464	847•4	1•591
708•6	1•323	770•1	1•464	877•2	1•623
718•5	1•355	783•2	1•496	897•6	1•655
738•0	1•404	785•7	1•497	910•7	1•666

TABLE XII.- COEFFICIENTS IN THE SPECIFIC CONDUCTANCE EQUATION: $\kappa = -a + bt - ct^2$, FOR VARIOUS MIXTURES OF POTASSIUM IODIDE AND POTASSIUM CHLORIDE

Mol.-% KCl	a	$10^2 b$	$10^6 c$	Temp. range, °C.
80•22	3•8914	1•2226	6•144	710–910
61•12	2•2493	0•8067	3•761	655–910
45•15	1•0837	0•4976	1•873	600–910
25•67	1•3927	0•5790	2•542	630–910
15•30	0•8419	0•4291	1•605	685–910
6•04	2•2372	0•7654	3•688	690–910

TABLE XIII.- COEFFICIENTS IN THE DENSITY EQUATION: $\rho = a' - b't$, FOR VARIOUS MIXTURES OF POTASSIUM IODIDE-POTASSIUM CHLORIDE

Mol.-% KCl	a'	$10^3 b'$	Temp. range, °C.
80·22	2·2736	0·6897	711–905
61·12	2·4985	0·7546	679–912
45·15	2·6838	0·8257	618–903
25·67	2·8736	0·8899	640–914
15·96	2·9143	0·8645	706–901
6·04	3·0305	0·9300	682–904

In Fig. 1 the specific conductance and the equivalent volume, at 800°, are shown as functions of composition; in Fig. 2, the equivalent conductance at 800° is similarly represented.

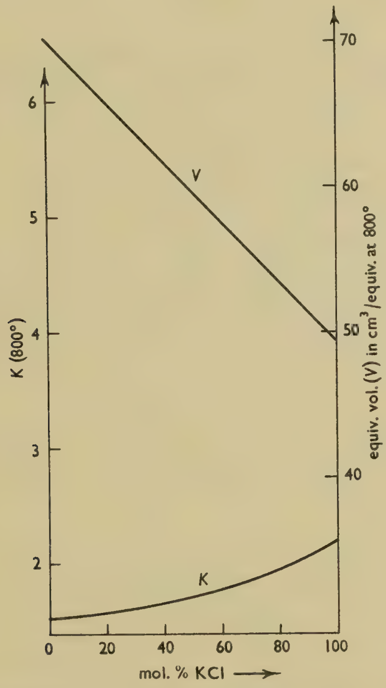


FIG. 1. SPECIFIC CONDUCTIVITY (K) AND EQUIVALENT VOLUME (V) IN THE SYSTEM KCl–KI AT 800°C.

The breakdown field-strength for potassium iodide is $0{\cdot}58 \times 10^6$ V./cm.[61-63] The dielectric constant of the solid is 5·58.[64] In the isomorphous series of solid solutions of potassium iodide and potassium bromide, the point of maximum lattice instability, characterized by minimum melting-point, is also the point of maximum dielectric loss at 10^6 cycles/sec.[65] An interesting method for the determination of dielectric constant consists in finding a mixture of two liquids, *a* and *b*, such that a cell containing this mixture shows unchanged capacity when the solid dielectric is introduced or withdrawn. With mixtures of benzene and nitrobenzene, the dielectric constant of potassium iodide was found to be 5·17,[66] in reasonable agreement with the value quoted above.[64]

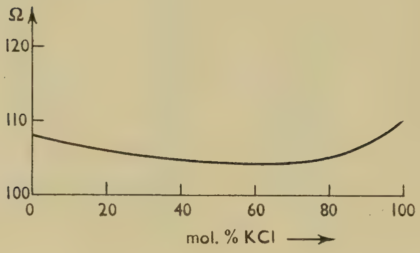


FIG. 2. EQUIVALENT CONDUCTIVITY IN THE SYSTEM KCl-KI AT 800°C.

From measurements of the heat of reaction of solid potassium iodide with solutions of the nitrates of bivalent mercury, cadmium and lead, thermodynamic functions relating to the formation of the complex ions HgI^+, CdI^+ and PbI^+ were determined.[67] The values are given in Table XIV.

TABLE XIV. - THERMODYNAMIC FUNCTIONS RELATING TO THE FORMATION OF SOME COMPLEX IODIDES

	ΔH, kg.-cal./mole	ΔG, kg.-cal./mole	ΔS, g.-cal./mole/°C.	S°, g.-cal./mole/°C.
HgI^+	−16·6	−18·4	6 ± 2	25 ± 2
CdI^+	−1·35	−4·2	9 ± 2	16 ± 2
PbI^+	−1·00	−3·13	7 ± 2	49 ± 2

Aqueous solutions of potassium iodide will now be considered. Densities and volume changes have been measured[68] at 18° with the results recorded in Table XV.

TABLE XV. - DENSITIES OF POTASSIUM IODIDE SOLUTIONS, AND VOLUME CONTRACTIONS OF SOLUTION, PER MOLE OF SALT
$t = 18°C.$

Molality	d_4^{18}	$-\delta V$ per mole, c.c.
23·077	1·015300	7·95
9·546	1·005569	8·30
7·286	1·003940	8·60
4·816	1·002138	8·60
0·000	0·998622	8·80 at infinite diln.

The density and partial volume of solutions of potassium iodide in water at 25° are listed in Table XVI.[69]

The molalities and densities of saturated solutions of potassium iodide at various temperatures are given in Table XVII.[70]

The critical temperatures of aqueous solutions of potassium iodide, and their increase over that of water, have been measured for dilute solutions, the results being given in Table XVIII.[71]

A review of the literature, and the redetermination of a number of values, gave the results shown in Table XIX for the solubility of potassium iodide in

TABLE XVI. - DENSITIES AND PARTIAL VOLUMES OF AQUEOUS SOLUTIONS OF POTASSIUM IODIDE, AT 25°C.

G. of KI per c.c.	Density	Partial vol. of solute
0	0·99708	0
0·01	1·00434	0·276
0·04	1·02601	0·280
0·09	1·06197	0·283
0·16	1·11208	0·287
0·25	1·17619	0·290
0·36	1·25414	0·293
0·49	1·34576	0·297
0·64	1·45087	0·300
0·81	1·56927	0·304
0·9025	1·63335	0·306
0·9500	1·66617	0·306

TABLE XVII. - SOLUBILITY OF POTASSIUM IODIDE IN WATER AT VARIOUS TEMPERATURES, AND DENSITY OF SATURATED SOLUTION

t, °C.	d_4^t	Molality
0	1·6673	7·72
35	1·7380	9·49
50·13	1·7600	10·18
92·18	1·8056	12·06

TABLE XVIII. - CRITICAL TEMPERATURES OF AQUEOUS SOLUTIONS OF POTASSIUM IODIDE

Molarity	t_c (soln.), °C.	t_c (soln.)-t_c (water)
0	374·2	-
0·04275	379·5	5·3
0·0855	382·8	8·6
0·171	389·2	14·9
0·342	399·0	25·8

TABLE XIX. - SOLUBILITY OF POTASSIUM IODIDE IN WATER BETWEEN 0° AND 240°C.

t, °C.	Solubility, g.KI/100g. water	t, °C.	Solubility, g.KI/100g. water	t, °C.	Solubility, g.KI/100g. water
0	129·1	90	198·6	170	263·7
10	136·8	100	206·4	180	272·9
20	144·5	110	214·3	190	282·6
30	152·2	120	222·3	200	292·9
40	159·9	130	230·3	210	303·4
50	167·6	140	238·5	220	314·3
60	175·3	150	246·7	230	326·0
70	183·0	160	255·0	240	338·4
80	190·8				

water between 0° and 240°.[72]

The mutual solubilities of potassium iodide and potassium sulphate may be calculated from an empirical equation applicable to two salts having a common ion:-

$$S_0 - S = KX^m,$$

where S_0 is the solubility of the saturating salt per unit volume and S its solubility in the presence of a quantity X of the second salt, m and K being constants. This relationship holds provided there is no formation of a double salt, mixed crystals or hydrates.[73]

The solubility of potassium iodide in water at 25° has been measured at pressures up to 10^4 atmospheres. Some results are recorded in Table XX.[74]

TABLE XX. - SOLUBILITY OF POTASSIUM IODIDE IN WATER, AT 25°C. UNDER HIGH PRESSURES

P, atm.	Wt.-% KI	P, atm.	Wt.-% KI	P, atm.	Wt.-% KI
1·0	59·7	4000	63·3	8000	67·0
1000	60·7	5000	63·9	9000	67·3
2000	61·7	6000	64·7	10000	68·4
3000	62·5	7000	65		

The compressibility of aqueous solutions of potassium iodide, at a constant pressure of 1000 bars, and at 25°C., is given in Table XXI as a function of concentration.[75]

TABLE XXI. - COMPRESSIBILITY OF AQUEOUS SOLUTIONS OF POTASSIUM IODIDE AT 25°, AND AT 1000 BARS

G. of KI per c.c. of soln.	Sp. compression of soln.
0	0·0394
0·09	0·0356
0·16	0·0330
0·25	0·0298
0·36	0·0266
0·49	0·0236
0·68	0·0204
0·81	0·0177
0·950	0·0158

The spontaneous crystallization of potassium iodide from supersaturated solution has been studied. Spontaneous crystallization was observed upon addition of much smaller crystals than Ostwald considered necessary.[76] In another study of supersaturation, for a number of salts, including potassium iodide, the relationship:-

$$\rho = \beta(\delta/\delta T \ln C_0)$$

was established, where β is a function of temperature, C_0 is the solubility, and ρ is defined by: $\rho = (C - C_0)/C_0$, C being the concentration of salt in the supersaturated solution. At 20°, β has the value 13·48, and ρ is calculated to be 0·043; the experimental value is 0·029.[77]

The refractive indices of dilute aqueous solutions of potassium iodide have been measured.[78] In Table XXII are recorded the normality (c), the difference (δn) in refractive index of solution and solvent, and the refractivity function ψ, defined as:-

$$\psi = 560{\cdot}68\delta n/c.$$

The refractive index of water, at temperature t°C., is given by:-

$$n_t^D = 1{\cdot}333000 - 10^{-5}[0{\cdot}124(t - 20) + 0{\cdot}1993(t^2 - 400) - 5 \times 10^{-6}(t^4 - 160{,}000)]$$

TABLE XXII. - REFRACTIVE INDICES OF AQUEOUS SOLUTIONS OF POTASSIUM IODIDE

$t = 18°$C.

10^3c	$10^6\delta n$	ψ	10^3c	$10^6\delta n$	ψ
2·0	42·98	12·05	0·7	17·3	13·6
1·6	37·4	12·59	0·6	14·6	13·6
1·33	31·2	13·12	0·5	12·1	13·6
1·00	24·3	13·61	0·3	7·3	13·6
0·9	21·5	13·39	0·2	4·9	13·6
0·8	19·4	13·60			

The molar refractivity, $[R]_D$, for potassium iodide has been measured at three temperatures:-

$$\begin{array}{rccc} t = & 6° & 18° & 30° \\ [R]_D = & 21·25 & 21·37 & 21·54. \end{array}$$

Within this temperature range $\delta R/\delta T$ has the value 0·012.[79]

The molar refractivity, dispersivity and rotativity of aqueous solutions of potassium iodide have been measured, at 25°, for magneto-optic rotation and dispersion. The results are given in Table XXIII.[80]

TABLE XXIII. - MOLAR REFRACTIVITY, $[R]_m$, MOLAR DISPERSIVITY, $[D]_m$, AND MOLAR ROTATIVITY, $[\Omega]_m$, FOR AQUEOUS POTASSIUM IODIDE, AT 25°

Molarity	$[R]_m$	$[D]_m$	$[\Omega]_m$
1	22·24	99·5	49·6
2	21·73	96·1	49·2
3	21·51	94·5	46·05

Wave-length = 5461A.

The diffusion coefficients of potassium iodide in aqueous solution have been measured at 25°. In Table XXIV, differential diffusion coefficients, D, are given; $\bar{D}°$ is the integral coefficient, defined by $\bar{D}° = 1/C\int_0^C \mathcal{D}.dC$, applying to a very short period of diffusion between solution of concentration C and pure water.[81]

TABLE XXIV. - DIFFERENTIAL AND INTEGRAL COEFFICIENTS OF DIFFUSION FOR POTASSIUM IODIDE SOLUTIONS, AT 25°C.

C, molarity	D, cm.^{2}sec.$^{-1}$	$\bar{D}°$ cm.^{2}sec.$^{-1}$	C, molarity	D, cm.^{2}sec.$^{-1}$	$\bar{D}°$ cm.^{2}sec.$^{-1}$
0	2·001	2·001	1·0	2·065	1·953
0·05	1·891	1·923	1·5	2·166	2·008
0·10	1·865	1·900	2·0	2·254	2·058
0·20	1·859	1·879	2·5	2·347	2·107
0·30	1·884	1·876	3·0	2·440	2·154
0·50	1·995	1·896	3·5	2·553	2·203
0·70	2·001	1·919			

The viscosity of 0·0012M. potassium iodide in water is 0·008947 ± 0·000001 c.g.s. units at 25°.[82]

Viscosity-temperature curves for potassium iodide solutions showed no break at the saturation temperature, from which it is deduced that there is no sudden change in viscosity when these solutions pass from the unsaturated to the supersaturated condition. The plot of η against $1/T$ is linear.[83]

Temperature coefficients of fluidity and of conductivity, for aqueous potassium iodide solutions, have been compared.[84] Their ratio was found to be approximately constant for different concentrations of the solution.

The dependence of surface tension on concentration for aqueous solutions of potassium iodide has been studied over the range 0·01 to 0·3M. The results may be expressed by $\Delta\gamma = 0{\cdot}2437(\alpha a + \frac{1}{2}\beta a^2)$, for a number of salt solutions; for potassium iodide, $\alpha = 7{\cdot}2579$, $\frac{1}{2}\beta = 2{\cdot}1503$, a being the activity of potassium iodide in the solution.[85] The surface tension has also been measured for solutions of potassium iodide in 2·03 mol.-% ethanol–water as solvent; the results are given in Table XXV.[86]

TABLE XXV. - SURFACE TENSIONS OF SOLUTIONS OF POTASSIUM IODIDE IN 2·03 MOL.-% ETHANOL–WATER AT 25°C.

KI concn., M.	γ dynes/cm.	$-d\gamma/dm$
0·99	54·97	0·64
1·99	53·96	1·01
2·98	53·28	0·58
3·98	53·15	0·13

The surface and interfacial tensions of potassium iodide solutions against *n*-hexane have been determined.[87] The organic solvent had b.p. 68·5°, d = 0·6691 g./c.c. The results are given in Table XXVI.

TABLE XXVI. - SURFACE TENSIONS γ OF AQUEOUS SOLUTIONS OF POTASSIUM IODIDE AND INTERFACIAL TENSIONS α AGAINST *n*-HEXANE t = 20°C.

KI concn., M.	γ dynes/cm.	α dynes/cm.
0·01	71·8	–
0·05	71·9	47·7
0·10	72·0	47·8
0·30	72·2	48·0

Assuming the interfacial tension between water and mercury to be 375·0 dynes/cm., at 20°, that of mercury and molar potassium iodide solution is 305·0 dynes/cm. A graph of interfacial tension against molarity, for potassium iodide solutions, is shown in Fig. 3.[88] The work of adhesion is 244·6 ergs/cm.^{2}

From a cryoscopic investigation, the hydration of the ions in 0·5M. potassium iodide corresponds to $KI,8{\cdot}6H_2O$.[89] The hydration number 8·0 was found from ebullioscopic studies of saturated aqueous solutions of potassium iodide.[90] The volume of hydration water is 54 c.c./mole for potassium iodide at infinite dilution.[91] The volume occupied by one molecule of hydrated potassium iodide, at various concentrations, has been calculated; the results at 18° are given in Table XXVII.[92]

TABLE XXVII. - VOLUME OCCUPIED PER MOLECULE BY HYDRATED POTASSIUM IODIDE AT 18°

Normality	Density	10^{23} V, c.c.	Normality	Density	10^{23} V, c.c.
4·0	1·47194	7·89	0·50	1·06019	7·10
2·0	1·23870	7·60	0·20	1·02426	6·19
1·0	1·12102	7·36	0·10	1·01218	5·12

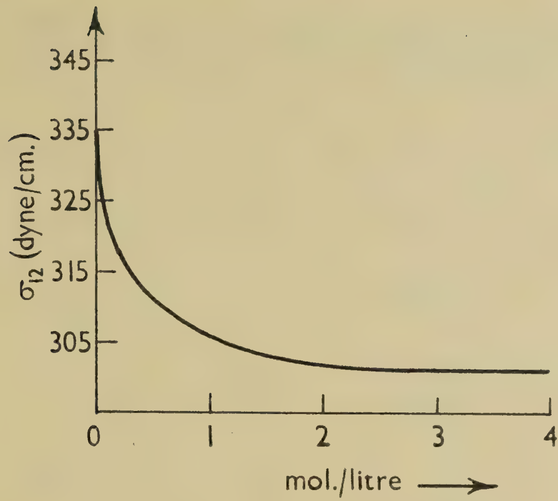


FIG. 3. THE INTERFACIAL TENSION (σ_{12}) BETWEEN Hg AND SOLUTIONS OF KI AS A FUNCTION OF CONCENTRATION

The radii of the ions has been estimated by extrapolation of the limiting volume occupied by the salt in the saturated solution to the hypothetical state in which no water is present.[93] The values $r_{K^+} = 1{\cdot}28$A. and $r_{I^-} = 2{\cdot}69$A., have been obtained for the rock-salt type crystal.

Hydration increases with decreasing volume of the cation, along a series of alkali-metal iodides.[94]

The relative lowering of vapour pressure of potassium iodide in aqueous solution at 23 ± 1° has been investigated, with the results recorded in Table XXVIII.[95]

TABLE XXVIII. - RELATIVE LOWERING OF VAPOUR PRESSURE FOR POTASSIUM IODIDE SOLUTIONS

C, molarity	$(p_{H_2O}-p_{soln.})/p_{H_2O}$	$(p_{H_2O}-p_{soln.})/C.p_{H_2O}$
4·600	0·145	0·032
3·000	0·091	0·030
2·000	0·063	0·032
1·000	0·030	0·030

The vapour pressures of concentrated aqueous solutions of potassium iodide up to saturation at 25° have been determined. The results are recorded in Table XXIX.[96]

TABLE XXIX. - VAPOUR PRESSURES AND MEAN-ION ACTIVITY COEFFICIENT OF CONCENTRATED AQUEOUS SOLUTIONS OF POTASSIUM IODIDE, AT 25°C.

Molality	p	$\gamma_\pm$	Molality	p	$\gamma_\pm$
0	23·752	1	3·0	21·516	0·656
0·1	23·686	0·917	4·0	20·681	0·707
0·2	23·620	0·813	5·0	19·822	0·765
0·4	23·486	0·740	6·0	18·966	0·839
0·6	23·348	0·687	7·0	18·082	0·937
1·0	23·072	0·649	8·0	17·190	1·049
1·5	22·702	0·633	8·938*	16·370	1·180

* Saturated solution

The vapour pressures of concentrated aqueous solutions of potassium iodide have been measured at temperatures from 110° to 200°C. The results are given in 11 tables, of which Fig. 4 is a summary.[96a]

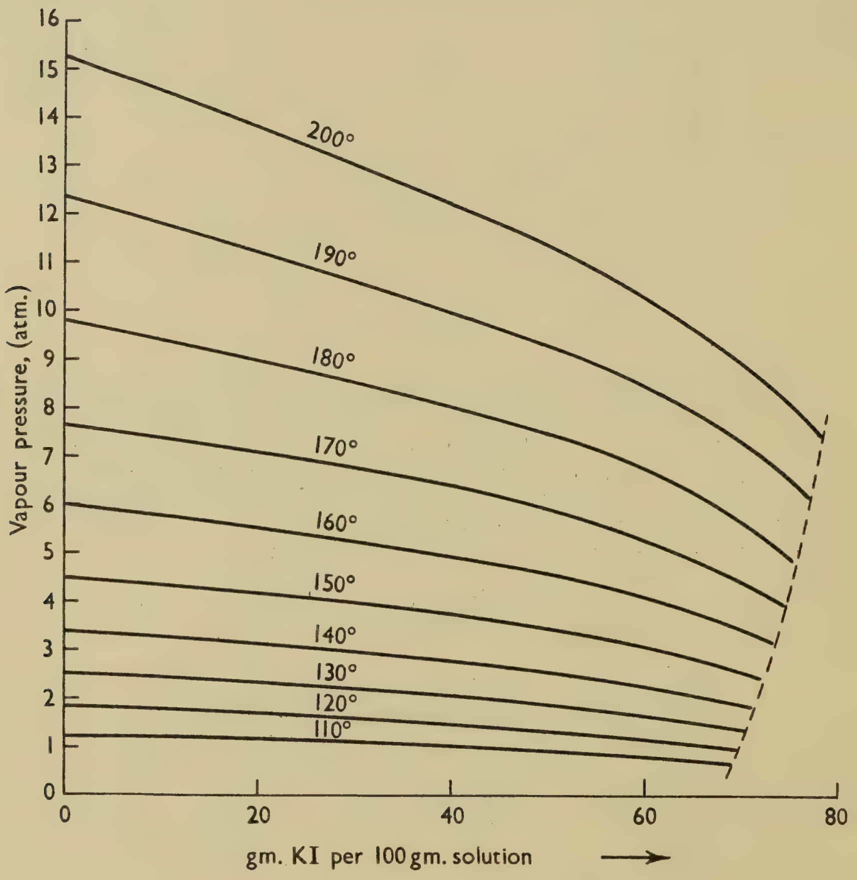


FIG. 4. VARIATION OF VAPOUR PRESSURE OF AQUEOUS KI SOLUTIONS WITH CONCENTRATION, AT TEMPERATURES FROM 110° TO 200°C. THE CURVE DENOTED BY --- REPRESENTS THE SOLUBILITY CURVE OF KI BETWEEN THESE TEMPERATURE LIMITS

The latent heat of vaporization for saturated solutions of potassium iodide between 30° and 40° has the mean value 10·31 kg.-cal./mole. The vapour pressures of supersaturated solutions may be calculated from the Clausius–Clapeyron equation in the form:-

$$\ln p = -L_v/RT + C,$$

where $C = 8{\cdot}7252$, and L_v is the appropriate latent heat of vaporization. No abrupt change in the vapour pressure–temperature curve occurred in the transition to the supersaturated region.[97]

The chemical potential of potassium iodide in aqueous solution at various concentrations has been determined from vapour-pressure data. The results are given in Table XXX; those obtained by an arithmetical interpolation are recorded under 'Method 1', those from a graphical solution under 'Method 2'.[98]

TABLE XXX. - CHEMICAL POTENTIAL OF POTASSIUM IODIDE IN AQUEOUS SOLUTIONS AT 25°

Molality	μ, g.-cal./mole Method 1	μ, g.-cal./mole Method 2
0	-	$-\infty$
0·05	-	-2776
0·10	-	-2156
0·2	-	-1530
0·5	-	-680
1·0	0	0
1·5	430	426
2·0	754	746
2·5	1015	1008
3·0	1239	1230
3·5	1437	1426
4·0	1611	1602
4·5	1772	1762
5·0	1921	1910
5·5	2059	2048
6·0	2186	2176
6·5	2309	2298
7·0	2427	2416
7·5	2540	2530
8·0	2649	2658
8·5	2752	2740
9·0	-	2838

Partial volumes of solute and solvent in potassium iodide solutions of varying concentration have been measured with the results given in Table XXXI.[99]

TABLE XXXI. - PARTIAL GRAM VOLUMES OF SOLUTE AND SOLVENT IN POTASSIUM IODIDE SOLUTIONS IN WATER AT 25°C.

Concn. of KI, g./c.c. solvent	Partial g. vol., solvent	Partial g. vol., solute
0·04571	1·00281	0·281
0·09185	1·00259	0·284
0·16686	1·00209	0·287
0·18466	1·00196	0·288
0·27000	1·00121	0·291
0·35477	1·00036	0·293
0·44465	0·99932	0·295
0·46084	0·99912	0·296
0·64032	0·99970	0·300
0·92435	0·99968	0·304

The partial molal volumes $(\overline{V})$ of aqueous solutions of potassium iodide have been measured by a magnetic float method; the results are shown below; $t =$ 25° C.:-[100]

Wt.-% KI	1·5801	3·0682	3·0888
V	45·95	46·12	46·12
Density	1·008626	1·019729	1·019882

The partial molal volume may be expressed by:-

$$V = 45{\cdot}44 + 1{\cdot}30m^{1/2},$$

where m is the molality of the solution.

The apparent partial molal heat capacities of potassium iodide in aqueous solutions have been evaluated. At 25° extrapolation to infinite dilution gives the value −30·2 g.-cal./degree, the rate of change with temperature being 0·3 g.-cal./degree over the range 18° to 25°C.[101] Heat data for aqueous solutions of potassium iodide are recorded in Table XXXII.[102]

TABLE XXXII. - HEATS OF SOLUTION AND DILUTION FOR AQUEOUS SOLUTIONS OF POTASSIUM IODIDE AT 25°, EXTRAPOLATED TO INFINITE DILUTION

Integral heat of solution,	−3·36 kg.-cal./mole
Differential heat of solution,	−2·60 kg.-cal./mole
Differential heat of dilution,	−123·2 g.-cal./mole H_2O

A new calorimetric procedure for measurement of heats of solution of salts has been developed; in this investigation, it was found that pre-melted potassium iodide showed a slightly increased heat of solution.[103]

An equation proposed for the evaluation of standard free energies of hydration of alkali halides gives, for potassium iodide, the value 138·7 kg.-cal./mole. The calculation[104] is based on thermodynamic data from the literature; such data have recently been collected.[105]

The heat of hydration of potassium iodide is 143 kg.-cal./mole.[106] The assumption of equal heats of hydration of K^+ and F^- ions, made by Bernal and Fowler,[107] is rejected, the authors choosing instead $\Delta H_h(Cs^+) = \Delta H_h(I^-)$; on this basis, they arrive at the individual heats of hydration: $\Delta H_h(K^+) = 80$, $\Delta H_h(I^-) = 63$ kg.-cal./mole.

Measurements of electroösmosis of potassium iodide in aqueous solution give the following results:-

Molarity	0·1	0·01	0·001	0·0001
Δ, cm./sec. per volt/cm.	0·068	2·52	19	403

The hydration of the ions is discussed.[108,109]

An electrocapillarity maximum is observed, for 0·5 N. potassium iodide solutions, at 0·475V., and for 0·5N. potassium chloride at 0·573V.; for an equi-molar mixture of these two solutions, the maximum occurs at 0·521V.[110]

Changes in electromotive force of such cells as Ag | KI(aq.) | Pt, on adding mercuric iodide or silver iodide, have been measured in order to study the formation of complex iodides; for example, the addition of mercuric iodide sufficient to saturate the potassium iodide solution changed the e.m.f. by 0·63V.[111]

At 18°, the equivalent conductivity at infinite dilution from aqueous solutions of potassium iodide is 130·82, the individual ionic mobilities being 65·36 (K^+) and 65·46 (I^-), respectively.[112] The specific conductivity at 50° ± 0·05° of aqueous solutions of potassium iodide containing agar-agar has been measured.[113] The results are given in Table XXXIII; the agar sol and gel, referred to in columns 2 and 3, contained 0·5 g. of agar-agar per 25 ml. of solution.

The equivalent conductivity and mean ionic activity coefficient for aqueous

TABLE XXXIII. - SPECIFIC CONDUCTIVITY OF AQUEOUS SOLUTIONS OF POTASSIUM IODIDE, CONTAINING AGAR-AGAR, AT 50°

Concn. of KI × 10^3 (mole/l.)	$10^5\kappa$		
	Aq. soln.	Agar sol.	Agar gel.
20	418·3	463·9	465·9
17·5	369·2	415·4	417·4
15	317·7	367·7	370·0
12·5	266·6	–	–
10	216·2	272·6	274·3
7·5	162·6	–	–
5	110·4	175·9	176·7
2·5	56·2	126·6	127·4
1·25	31·35	101·7	102·5
0·625	15·50	–	–

solutions of potassium iodide have been measured with the results given in Table XXXIV.[114]

TABLE XXXIV. - EQUIVALENT CONDUCTIVITY AND ACTIVITY COEFFICIENT OF AQUEOUS POTASSIUM IODIDE AS A FUNCTION OF CONCENTRATION AT 25°

Molarity	0·002	0·01	0·05	0
Λ	146·8	142·8	135·6	151·2
$f_\pm$	0·971	0·942	0·894	1·0

In Table XXXV the specific conductivity of aqueous solutions of potassium iodide at 0° and 26° is recorded.[115]

TABLE XXXV. - SPECIFIC CONDUCTIVITY OF AQUEOUS SOLUTIONS OF POTASSIUM IODIDE

Molarity	$10^5\kappa$	
	0°	26°
0·1	7·48	2258
0·01	7·99	2304
0·001	9·31	2312

Extensive determinations of equivalent conductivity of aqueous solutions of potassium iodide have been made at several temperatures; the results are given in Table XXXVI.[116] In this Table δ represents the deviation $100(\Lambda^\circ_{\text{calc.}} - \Lambda^\circ_{\text{obs.}})$.

From the measured equivalent conductivities of aqueous potassium iodide solutions at 25°, limiting values for infinite dilution have been calculated from the equation:-

$$\Lambda^\circ = \frac{(\Lambda + 2\beta c^{1/2})}{(1 - \theta c^{1/2})}\ ,$$

where $\beta = 30{\cdot}09$, and $\theta = 0{\cdot}2289$. Table XXXVII gives the results obtained.[117]

The limiting ionic mobilities are 73·50 and 76·97, for K^+ and I^-, respectively.

The increase in conductivity of potassium iodide solutions due to greatly increased field-strength (the Wien effect[118]) is shown in Fig. 5.[119]

The effect of iodine on the specific conductivities of potassium iodide solutions has been studied at temperatures between 15° and 50°,[120] the results

TABLE XXXVI. - EQUIVALENT CONDUCTIVITIES OF AQUEOUS SOLUTIONS OF POTASSIUM IODIDE

t = 5°C.			t = 15°C.		
1000c	Λ	δ	1000c	Λ	δ
0	95·32	–	0	121·83	–
0·9822	93·60	0	0·9068	119·67	0
1·6750	93·09	+1	2·0018	118·68	–1
2·7735	92·50	+1	3·8038	117·57	0
4·8149	91·69	+1	5·7454	116·68	0
6·8829	91·06	0	7·4005	116·08	0
8·7610	90·60	0	9·2226	115·50	0
13·2357	89·71	0	12·6653	114·59	0
18·3163	88·92	+2	16·9408	113·62	–2
t = 25°C.			t = 35°C.		
0	150·34	–	0	180·60	–
1·3835	147·00	–1	1·2633	176·63	–2
1·9682	146·38	0	2·4626	175·13	0
3·8674	144·95	–3	3·9050	173·83	+1
3·9858	144·85	0	5·9058	172·42	+1
5·8982	143·78	–1	7·4725	171·57	+3
6·6355	143·42	0	9·3285	170·61	+1
7·2957	143·13	–1	13·2222	169·02	–1
8·9114	142·47	0	17·8220	167·51	–2
8·9277	142·45	+1			
11·7214	141·50	–2			
15·9940	140·27	–1			
t = 45°C.			t = 55°C.		
0	212·13	–	0	244·73	–
1·6373	206·70	–2	1·3527	238·84	–1
2·9458	204·92	+3	3·2462	235·83	+1
3·7024	204·15	+1	4·9941	233·90	+1
5·7514	202·37	+2	6·9704	232·17	–1
9·1338	200·17	+2	8·6627	230·89	+1
13·3067	198·10	+2	10·6530	229·61	+1
17·3469	196·52	–1	12·8409	228·39	–2
			16·1548	226·75	0

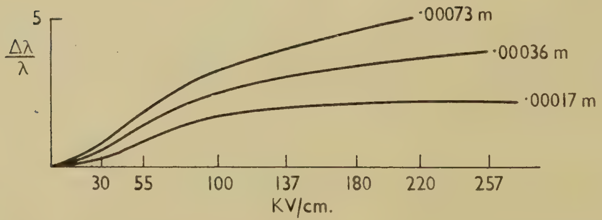


FIG. 5. SPECIFIC INCREASE IN CONDUCTIVITY (λ) AS A FUNCTION OF APPLIED FIELD STRENGTH FOR DIFFERING MOLARITIES (m)

TABLE XXXVII. - EQUIVALENT CONDUCTIVITIES OF POTASSIUM IODIDE SOLUTIONS AND CALCULATED LIMITING VALUES AT INFINITE DILUTION

$t = 25°$

$10^4 c$	Λ	$\Lambda°$
5	148·42	150·54
10	147·60	150·59
20	146·48	150·71
50	144·38	151·08

being given in Table XXXVIII. The results are interpreted in terms of formation of the less mobile I_3^- ion.

TABLE XXXVIII. - SPECIFIC CONDUCTIVITIES OF POTASSIUM IODIDE SOLUTIONS (40% BY WEIGHT) CONTAINING IODINE

% Iodine	κ	t°C.	κ	t°C.
0	0·32	19	0·4	35
3·0	0·32	20	0·44	45
5·9	0·38	35	0·31	20

Transference numbers for aqueous solutions of potassium iodide have been determined at 25°:-[121]

Molarity	0·01	0·02	0·05	0·10	0·20
t_{K^+}	0·4884	0·4883	0·4882	0·4883	0·4887

A more extended series of results is shown in Table XXXIX.[122]

TABLE XXXIX. - TRANSPORT NUMBERS AND ACTIVITY COEFFICIENTS FOR AQUEOUS POTASSIUM IODIDE SOLUTIONS ($t = 25°$C.)

Molality	$\gamma_\pm$	t_{K^+}	Molality	$\gamma_\pm$	t_{K^+}
0·002	0·992	0·4983	0·200	0·721	0·4917
0·005	0·938	0·4979	0·300	0·709	–
0·010	0·920	0·4974	0·500	0·666	0·4878
0·020	0·869	0·4968	1·000	0·674	–
0·050	0·810	0·4954	2·000	0·645	–
0·100	0·772	0·4940			

Activity coefficients for potassium iodide solutions have been determined from the electromotive force of the cell:-

$$\mathrm{Ag} \mid \mathrm{AgI} \mid \mathrm{KI}(m) \mid \mathrm{K{-}Hg} \mid \mathrm{KI}(m') \mid \mathrm{AgI} \mid \mathrm{Ag}$$

The results[123] are shown below:-

Molarity	0·1	0·3	0·5	1·0	2·0
$\gamma_\pm$	0·775	0·715	0·678	0·649	0·646

Activities have also been calculated from isopiestic data, the results comparing favourably with those from e.m.f. measurements, as is shown by comparing the results in Table XL[124] with those of refs. 122 and 123.

TABLE XL. - MEAN ION ACTIVITY COEFFICIENTS FOR AQUEOUS SOLUTIONS OF POTASSIUM IODIDE AT 25°

Molality	$\gamma_\pm$	Molality	$\gamma_\pm$	Molality	$\gamma_\pm$
0·1	0·776	1·0	0·646	3·0	0·657
0·2	0·731	1·5	0·639	3·5	0·667
0·3	0·704	2·0	0·641	4·0	0·678
0·5	0·675	2·5	0·649	4·5	0·692
0·7	0·659				

The activity of the solvent in aqueous solutions of potassium iodide has been determined at several temperatures by the vapour-pressure method.[125] For a solution containing 152 g. per 100 g. of water, the results below were obtained:-

Temperature, °C.	35	40	45	50
a_{solvent}	0·720	0·711	0·711	0·735

From a study of centrifugal-e.m.f. cells, with potassium iodide-iodine as electrolyte, it is concluded that in these solutions two atoms of iodine combine with one iodide ion to form the I_3^- ion.[126]

The Soret coefficient for potassium iodide has been determined at several temperatures,[127] the concentration being 0·05N.:-

t°C. =	30	40	50	60
$10^3 S$ =	−0·14	0·93	1·75	2·40

These results were determined with a temperature difference of 17° between the two vessels. For alkali halides, e.g. potassium iodide, the Soret coefficient of the electrolyte is the sum of the values for its ions, within the experimental error, for the concentration chosen.

The dielectric constant of dilute solutions of potassium iodide has been determined at 25°, and the results are given in Table XLI.[128]

TABLE XLI. - DIELECTRIC CONSTANT OF DILUTE SOLUTIONS OF POTASSIUM IODIDE AT 25°C.

Molarity	$D_{\text{soln.}}$	$D_{\text{soln.}} - D_{\text{water}}$
0	78·54	–
10^{-4}	78·82	0·04
3×10^{-4}	78·93	0·06
10^{-3}	78·87	0·12

Values of the magnetic susceptibility of potassium iodide in aqueous solutions at 20° are given below:-[129]

Wt.-% KI	33·9	43·55	57·23	100
$-10^7\psi$	6·12	5·81	5·39	3·97

The solubility of potassium iodide has been determined in potassium hydroxide solutions at 20°, as recorded in Table XLII.[130]

TABLE XLII. - SOLUBILITY OF POTASSIUM IODIDE IN AQUEOUS POTASSIUM HYDROXIDE SOLUTION

Molarity		Molarity		Molarity		Molarity	
KOH	KI	KOH	KI	KOH	KI	KOH	KI
14·35	0·556	8·814	1·541	5·853	2·634	2·405	4·454
13·28	0·651	8·161	1·733	5·816	2·650	1·860	4·818
12·51	0·759	7·050	2·171	4·753	3·145	1·358	5·132
11·05	0·981	6·624	2·292	4·111	3·484	0·783	5·539
10·53	1·107	6·453	2·369	4·000	3·525	0	6·089

Similar results for solubilities in sodium hydroxide solution at 20° are given in Table XLIII.[131]

Turning to the properties of potassium iodide in non-aqueous solutions, its solubility in liquid ammonia at 0°C. is 184 g. per 100 g. of ammonia.[132]

From vapour-pressure measurements the activity coefficient of potassium iodide in liquid sulphur dioxide has been determined with the results shown in

TABLE XLIII. - SOLUBILITY OF POTASSIUM IODIDE IN AQUEOUS SODIUM HYDROXIDE SOLUTION

Molarity		Molarity		Molarity		Molarity	
NaOH	KI	NaOH	KI	NaOH	KI	NaOH	KI
16·50	1·03	10·06	1·81	5·20	3·35	2·57	4·58
16·22	1·03	8·68	2·18	5·04	3·44	1·34	5·26
13·45	1·29	7·77	2·42	4·77	3·53	0·95	5·48
10·80	1·67	6·78	2·75	3·60	4·06	0	6·09

TABLE XLIV. - ACTIVITY COEFFICIENTS OF POTASSIUM IODIDE IN LIQUID SULPHUR DIOXIDE AT 25°C.

$p_{SO_2} = 290{\cdot}63$ cm.

Molality	N_{solute}	$\gamma_\pm$	Molality	N_{solute}	$\gamma_\pm$
0·0001	0·0000128	0·989	0·50	0·0602	0·0097
0·0005	0·0000641	0·655	0·60	0·07138	0·00838
0·001	0·000128	0·471	0·70	0·08230	0·00742
0·005	0·000640	0·186	0·80	0·09297	0·00670
0·01	0·00120	0·094	0·90	0·10339	0·00615
0·05	0·006365	0·0528	1·0	0·11357	0·00577
0·10	0·01265	0·0335	1·5	0·16120	0·00477
0·20	0·02498	0·0204	2·0	0·20397	0·00468
0·30	0·03701	0·0148	2·5	0·24260	0·00492
0·40	0·04875	0·0117	3·0	0·27765	0·00524

Table XLIV.[133]

The electrical conductivity of solutions of potassium iodide in liquid phosphorus oxychloride has been measured. The solubility of potassium iodide is 1·71 g./l. and the specific conductivity of the saturated solution is $1{\cdot}2 \times 10^{-4}$ ohm^{-1}cm.$^{-1}$.[134] The specific conductivity of potassium iodide in aluminium iodide as solvent at 200° is recorded in Table XLV, and the temperature variation for a 20 mol.-% solution in Table XLVI.[135]

TABLE XLV. - SPECIFIC CONDUCTIVITY OF POTASSIUM IODIDE SOLUTIONS IN ALUMINIUM IODIDE AT 200°C.

Mol.-% KI	$10^5\kappa$	Mol.-% KI	$10^5\kappa$	Mol.-% KI	$10^5\kappa$	Mol.-% KI	$10^5\kappa$
0·83	22·05	5·12	459·2	23·90	4303	37·03	7945
1·58	55·16	7·78	842·1	25·47	4767	41·33	9847
3·11	202·4	14·78	2223	27·01	5161	44·17	11160
3·68	267·7	21·78	3907	31·88	6546	46·50	12110

TABLE XLVI. - TEMPERATURE VARIATION OF SPECIFIC CONDUCTIVITY OF 20 MOL.-% POTASSIUM IODIDE IN ALUMINIUM IODIDE AS SOLVENT

t°C.	$10^5\kappa$	t°C.	$10^5\kappa$	t°C.	$10^5\kappa$	t°C.	$10^5\kappa$
190	3373	230	5074	260	6472	290	7835
200	3821	240	5584	270	6880	300	8431
210	4232	250	5920	280	7453	310	8784
220	4662						

The molecular conductivity of potassium iodide in aluminium iodide has been calculated from the data of Table XLVI, and is given for each dilution, ϕ, in Table XLVII;[135] it is observed that molar conductivity decreases with increasing dilution, and this is ascribed to complex formation in this system.

TABLE XLVII. - MOLAR CONDUCTIVITY OF POTASSIUM IODIDE IN ALUMINIUM IODIDE AS SOLVENT, AT 200°

ϕ, c.c./mole KI	Λ_M	ϕ, c.c./mole KI	Λ_M
182·2	22·06	499·9	19·25
201·3	22·46	779·6	17·31
221·0	21·76	1561	13·14
256·5	20·38	2420	11·11
312·7	20·41	3396	9·09
385·3	19·89	4044	8·19
414·1	19·74	8053	4·44
447·4	19·53	15470	3·41

The solubility of potassium iodide in methanol–water mixtures at 25° has been measured, and is recorded in Table XLVIII.[136]

TABLE XLVIII. - SOLUBILITY OF POTASSIUM IODIDE IN METHANOL–WATER MIXTURES AT 25°

Wt.-% MeOH	Mol. fraction MeOH	Molality KI
0	0	8·962
20·00	0·1233	6·776
40·82	0·2795	4·845
60·21	0·4597	3·333
72·39	0·5959	2·473
80·03	0·6927	1·970
89·79	0·8311	1·412
94·76	0·9103	1·187
100·0	1·000	0·965

An attempt is made to interpret these results in terms of the variation in dielectric constant of the solvent.

The solubility in methanol–water and ethanol–water mixtures has been measured at 10° and 20°.[137] The results are shown, in comparison with those for potassium bromide, in Figs. 9 and 10.

The effect of sodium and magnesium iodides on the solubility of potassium iodide in ethanol has been investigated; the solubility of the potassium iodide decreases as the concentration of the added salt increases.[138] The results are given in Table XLIX.

TABLE XLIX. - SOLUBILITY OF POTASSIUM IODIDE IN ETHANOL IN THE PRESENCE OF SODIUM AND MAGNESIUM IODIDES

$t = 25°$ C.

G. NaI/100g. EtOH	G. KI/100g. EtOH	d_4^{25}
0	1·824	0·7970
4·248	1·268	0·8215
7·091	0·9988	0·8378
9·065	0·8878	0·8502
15·84	0·6752	0·8921
27·68	0·442	0·9614
42·8	0·19	1·0500

continued on the following page

TABLE XLIX (continued)

G. MgI_2/100g. EtOH	G. KI/100g. EtOH	d_4^{25}
0	1·824	0·7970
2·777	1·502	0·8161
3·20	1·513	0·8202
5·53	1·578	0·8317
6·017	1·56	0·8420
8·809	1·393	0·8634
14·41	1·195	0·9037
17·82	1·116	0·9182

The mean ion activity coefficient of the solute, and the activity of the solvent, have been measured for potassium iodide solutions in ethanol;[139] the results are listed in Table L, and apply at the boiling-point of the solvent.

TABLE L. - MEAN ION ACTIVITY COEFFICIENTS OF POTASSIUM IODIDE IN ETHANOL SOLUTION AND THE ACTIVITY OF THE SOLVENT

t = 78·8°C.

Molality	$\gamma_\pm$	a_{EtOH}
0·01	0·1446	0·9989
0·02	0·1035	0·9978
0·05	0·0639	0·9947
0·075	0·0539	0·9920
0·100	0·0469	0·9894
0·125	0·0420	0·9867
0·150	0·0382	0·9841

The results of solubility determinations in some organic solvents, at 18° and 25°, are given in Table LI.[140]

TABLE LI. - SOLUBILITY OF POTASSIUM IODIDE IN SOME ORGANIC SOLVENTS

Solvent	Temperature	Density	Solubility, g./100g.	Solubility, g.-mol./l.
Methanol	18°	0·900	16·4	0·765
Methanol	25°	0·898	17·0	0·785
Acetonitrile	18°	0·798	2·1	0·10
Acetonitrile	25°	0·795	2·11	0·10
Formic acid	18°	1·479	35·0	2·31
Formic acid	25°	1·476	35·3	2·32

The solubility of potassium iodide in acetone at various temperatures has been measured, as shown in Table LII. It is concluded that below −57·5° the solute is most probably $KI,5C_3H_6O$; over the range of temperatures recorded, the heat of solvation varies from −14·6 to −18·0 kg.-cal./mole.[141]

The solubility relative to that in water has been determined for potassium iodide in aqueous acetone; the results are given in Table LIII.[142]

The solubility of potassium iodide in aqueous glycol and the densities of these solutions at 30° are given in Table LIV.[143]

The specific volume of potassium iodide in glycol solutions has been measured, at 25°, with the results shown below:-[144]

Wt.-fraction KI	0·06857	0·13469	0·20924	0·28526
Sp. vol., ml.	0·85918	0·81924	0·77460	0·72932

The viscosity of solutions of potassium iodide in aqueous ethanol solutions

TABLE LII. - SOLUBILITY OF POTASSIUM IODIDE IN ACETONE

Temperature, °C.	Solubility, wt.-%	Temperature, °C.	Solubility, wt-%
-78·5	4·15	-26·3	3·87
-64·4	6·84	4·62	2·02
-58·5	9·00	25·0	1·33
-57·6	9·79	26·54	1·30
-56·4	9·2	48·75	0·89
-44·8	6·08	54·50	0·84

TABLE LIII. - SOLUBILITY OF POTASSIUM IODIDE IN AQUEOUS ACETONE RELATIVE TO THAT IN WATER

Acetone (g./100g. soln.)	Rel. soly.	Acetone (g./100g. soln.)	Rel. soly.
0	1·0	50	1·0
10	0·99	60	1·03
20	0·98	70	1·09
30	0·97	80	1·02
40	0·98		

TABLE LIV. - SOLUBILITY OF POTASSIUM IODIDE IN AQUEOUS GLYCOL AND DENSITIES OF SOLUTIONS AT 30°

Glycol (wt.-%)	Water (wt.-%)	KI (wt.-%)	Density
0	39·49	60·31	1·7302
8·96	35·14	55·90	1·6655
19·26	29·76	50·98	1·6031
32·27	22·35	45·38	1·5395
51·57	10·16	38·27	1·4687
66·41	0	33·57	1·4272

TABLE LV. - VISCOSITY OF ETHANOL-WATER SOLUTIONS OF POTASSIUM IODIDE, AT 20°, 40° AND 60°

G. KI/100ml. soln.	Sp. gr. of solvent (EtOH–H_2O)	t°C.	$10^2\eta$, c.g.s. units
12·021	0·9841	20	1·2605
		40	1·2365
		60	1·1972
39·007	0·9842	20	1·1217
		40	1·1818
		60	1·2247
12·018	0·9282	20	2·4917
		40	2·1420
		60	1·872
39·004	0·9275	20	2·1143
		40	2·0200
		60	1·9408
6·001	0·8248	20	1·7979
		40	1·7416
		60	1·6445

has been determined,[145] as recorded in Table LV.

In Table LVI, the densities and viscosities of solutions of potassium iodide in methanol are listed.[146]

The relative viscosity of more concentrated solutions of potassium iodide

TABLE LVI. - DENSITIES AND VISCOSITIES OF METHANOL SOLUTIONS OF POTASSIUM IODIDE AT 25°C.

Molality	η, c.g.s. units	Density
0.0812	0.00569	0.79597
0.0916	0.00571	0.79830
0.1643	0.00588	0.80601
0.1930	0.00595	0.81018
0.2577	0.00609	0.81701
0.4951	0.00667	0.84660

TABLE LVII. - RELATIVE VISCOSITIES OF METHANOL SOLUTIONS OF POTASSIUM IODIDE, η_S/η_0

G. solute/100g. MeOH	t = 35°	40°	45°	50°C.
10.0	1.261	1.250	1.248	1.251
20.0	–	1.459	1.453	1.448

in methanol is given in Table LVII.[147]

The change of relative viscosity with temperature has been studied for solutions of potassium iodide in methanol and in glycerol.[148] The results obtained, together with viscosity-concentration and density-concentration relationships for these solutions, are shown in Figs. 6, 7 and 8. The Grüneisen

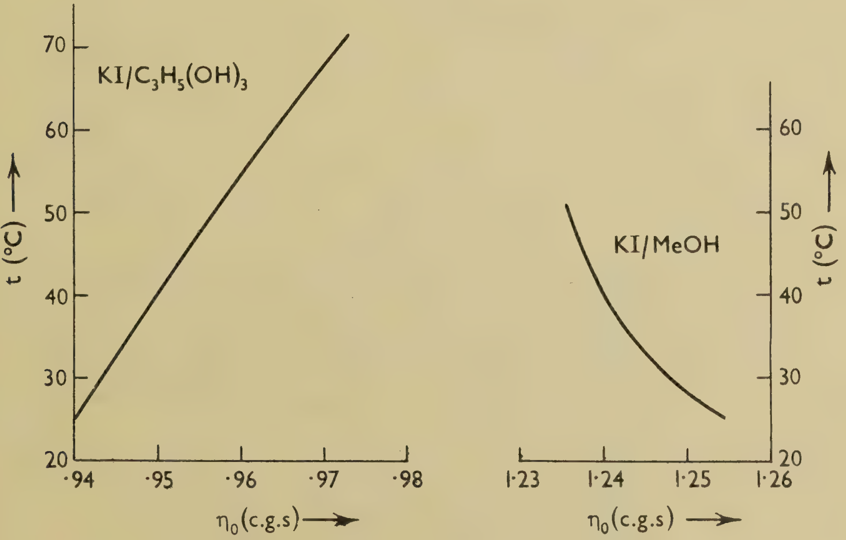


FIG. 6. THE VARIATION OF RELATIVE VISCOSITY WITH TEMPERATURE FOR APPROXIMATELY 0.5 MOLAR SOLUTIONS OF KI IN GLYCEROL AND METHANOL

function, $(\eta_0 - 1)/c$, where η_0 is the relative viscosity at concentration c, is tabulated for potassium iodide solutions in glycerol and in methanol in Table LVIII.[148]

The Table shows a minimum in G for solutions in glycerol, such as was observed by Grüneisen for aqueous salt solutions; it is concluded that, in glycerol solutions, potassium iodide behaves as a 'water-electrolyte'.

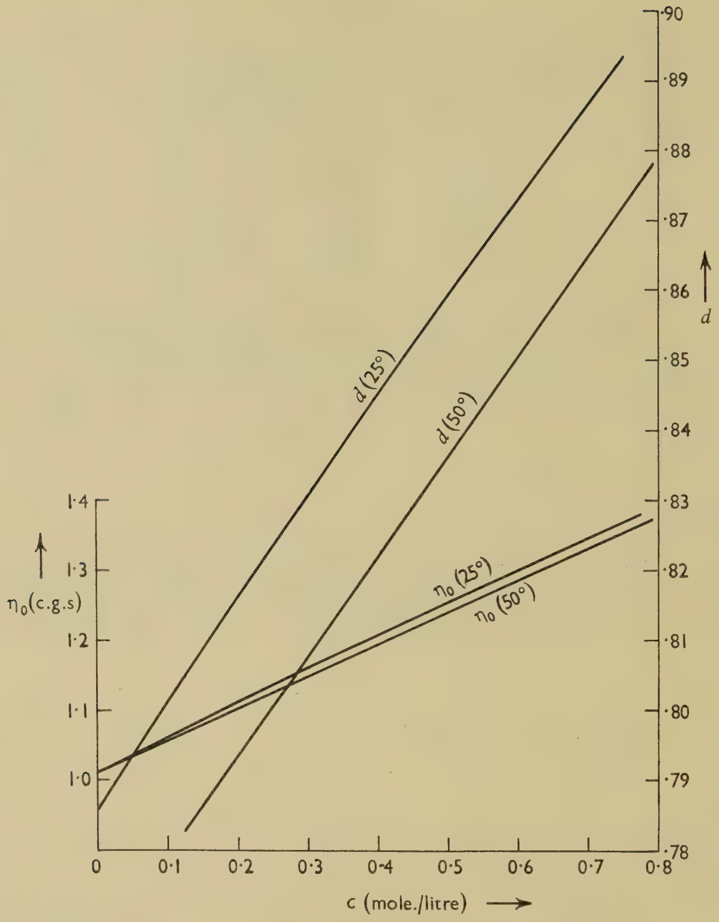


FIG. 7. THE VARIATION OF RELATIVE VISCOSITY (η_0) AND DENSITY (d) WITH MOLARITY OF KI IN MeOH SOLUTION AT 25° AND 50°C.

TABLE LVIII. - THE GRÜNEISEN FUNCTION, G, FOR METHANOL AND GLYCEROL SOLUTIONS OF POTASSIUM IODIDE AT 25°C.

KI–Methanol			KI–Glycerol		
η_0	c	G	η_0	c	G
1·05	0	–	1·008	0	–
1·11	0·2	0·550	0·980	0·2	−0·100
1·205	0·4	0·513	0·952	0·4	−0·120
1·300	0·6	0·500	0·926	0·6	−0·123
1·393	0·8	0·491	0·900	0·8	−0·125
			0·876	1·0	−0·124
			0·855	1·2	−0·120
			0·836	1·4	−0·117
			0·818	1·6	−0·114
			0·803	1·8	−0·109

No minimum is observed, within the concentration range studied, for methanol solutions, and the viscosity–temperature relationship is that of a 'water non-electrolyte'. The surface tension of solutions of potassium iodide in

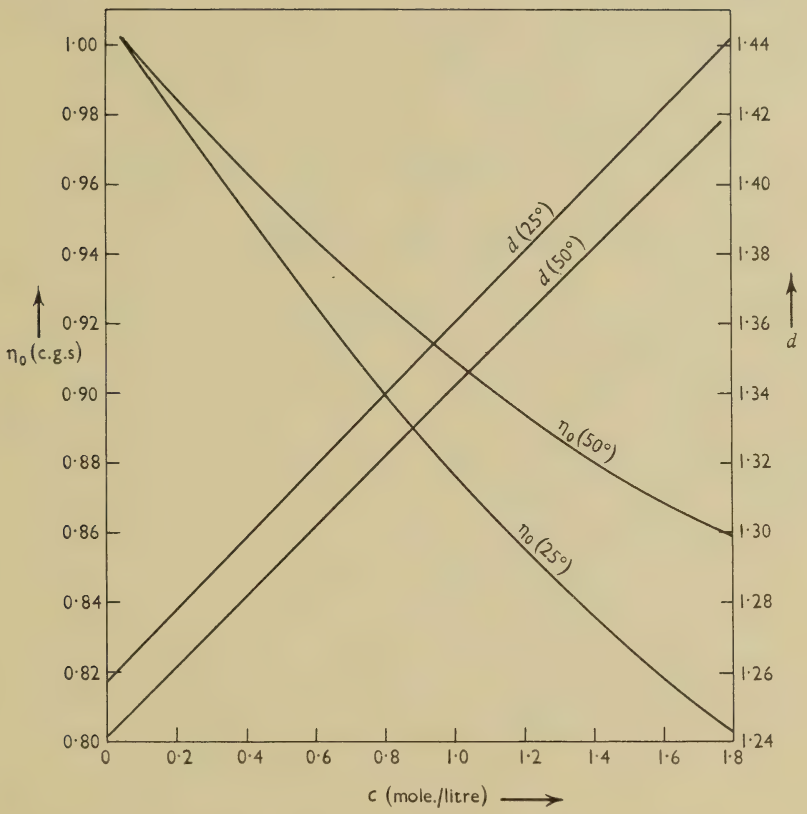


FIG. 8. THE VARIATION OF RELATIVE VISCOSITY (η_0) AND DENSITY (d) WITH MOLARITY OF KI IN GLYCEROL SOLUTION AT 25° AND 50°C.

ethanol–water (2·03 mol.-% ethanol) has been measured, with the results listed in Table LIX.[149]

TABLE LIX. - SURFACE TENSION OF SOLUTIONS OF POTASSIUM IODIDE IN A 2·03 MOL.-% ETHANOL–WATER MIXTURE AT 25°C.

Molality	γ, dynes/cm.	$d\gamma/dm$
0·99	54·97	0·64
1·99	53·96	1·01
2·98	53·28	0·58
3·98	53·15	0·13

(γ_{solvent} = 55·61 dynes/cm.)

The compressibility of potassium iodide solutions in glycol is recorded in Table LX.[150]

Potassium iodide behaves as an ideal electrolyte in cryoscopic measurements of solutions in anhydrous hydrogen cyanide.[151] The solvent has a

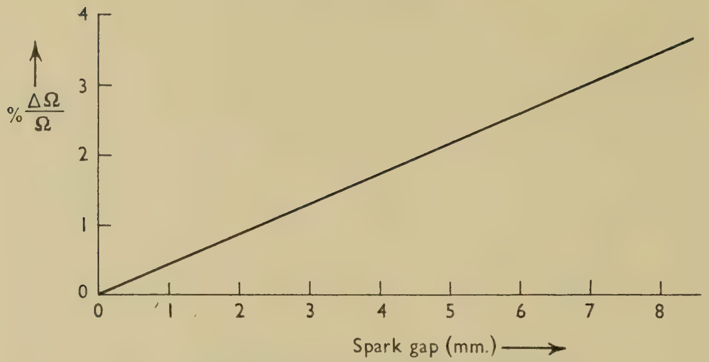


FIG. 9. WIEN EFFECT FOR KI IN ACETONE

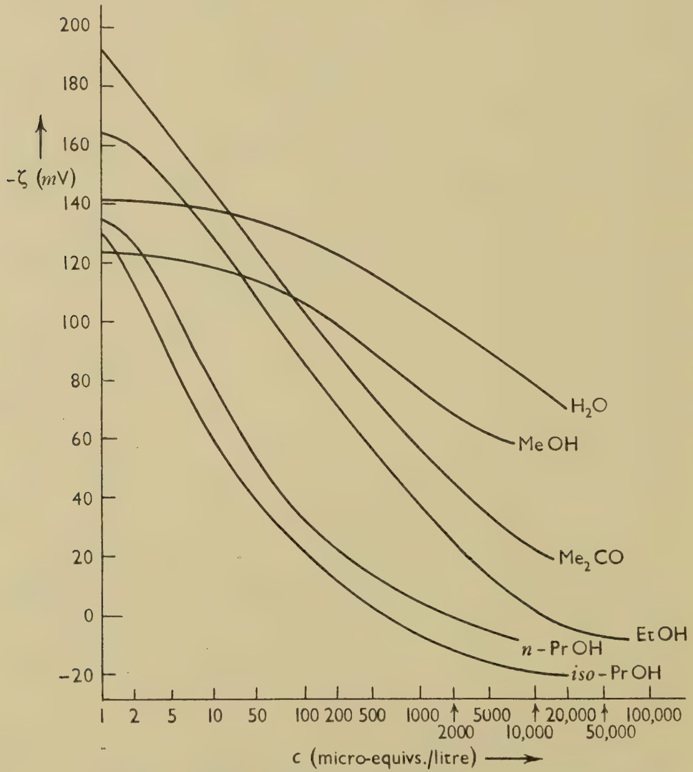


FIG. 10. VARIATION OF 'ZETA' POTENTIALS OF KI SOLUTIONS IN ORGANIC SOLVENTS WITH CONCENTRATION

TABLE LX. - COMPRESSIBILITY OF POTASSIUM IODIDE SOLUTIONS IN GLYCOL AT 25°C.

Wt. fraction KI	$10^4\ d\phi/dp$	$10^4\ d\theta/dp$
0·06857	20	304
0·13469	18	294
0·20924	8	285
0·28526	0	276

(ϕ = apparent volume, θ = relative volume change) freezing point of 259·9°K., and ideality is observed up to concentrations of 0·139M. KI, with a freezing-point depression of 0·688°. The heat of solution of potassium iodide in liquid ammonia at −33° is 5·90 kg.-cal./mole, compared with the value −5·11 for water.[152] Some molar heats of solution are given in Table LXI.[153]

TABLE LXI. - MOLAR HEAT OF SOLUTION OF POTASSIUM IODIDE IN LIQUID AMMONIA AT −33·4°C.

$\sqrt{m}$	$\Delta H_{soln.}$, kg.-cal.	$\sqrt{m}$	$\Delta H_{soln.}$, kg.-cal.
0·896	6·47	0·489	7·82
0·704	6·52	0·440	7·82
0·696	6·53	0·403	7·80
0·587	6·96	0	7·82

Adiabatic compressibilities have been determined for concentrated solutions of potassium iodide in liquid ammonia, at temperatures between −30° and −70°, by sound-velocity measurements. The compressibility β is given, in the appropriate units, by $\beta = 1/c^2\rho$, where c is the velocity of sound in the solution, and ρ its density. Over the range of mole-ratio $\log_{10}$ (NH$_3$)/(KI) = 1·5-2·5, $10^{12}\beta$ = 40–47.[153a]

The molar heats of solution of potassium iodide in methanol and ethanol are +0·647 and −0·740 kg.-cal., respectively, at infinite dilution.[154] The heats of transfer from solvent a to solvent b, in kg.-cal./mole,[154] are given below:-

a:	MeOH	Water	Water
b:	EtOH	EtOH	MeOH
ΔH:	−1·3	+4·3	+5·7

The heat of dissociation of potassium iodide in benzonitrile is −3 kg.-cal./mole, and ΔH of solvation is estimated to be +233 kg.-cal./mole. The mean value of the dissociation constant at various temperatures is given below:-[155]

Temperature	0°	25°	40°	50°	70°
$10^3 K_{mean}$	16	11	7·2	6·6	6·0

The following heats of solution of potassium iodide in formamide have been measured; the results are in g.-cal./mole, at 25°C.:-[156]

Final concn. (molality)	0·144	0·275
ΔH_s(integral)	−1053	−1071

In general, for molality m, $\Delta H_S = -1000 - 257m$ within the range 0·1–0·4 molal KI.

The equivalent conductivity of potassium iodide solutions in liquid hydrazine, at 25°, has been determined; the results may be represented by the equation:-

$$\Lambda_c = 132{\cdot}7 - 140c^{1/2}$$

as shown in Table LXII.[157]

TABLE LXII. - EQUIVALENT CONDUCTIVITY OF POTASSIUM IODIDE IN LIQUID HYDRAZINE AT 25°

$10^4 c$	Λobs.	Λcalc.	$10^4 c$	Λobs.	Λcalc.
4·409	130·6	129·8	36·68	124·1	124·2
15·44	127·2	127·2	43·47	123·6	123·5
17·78	126·8	126·8	69·29	120·3	121·1
28·32	124·8	125·2	135·9	116·3	116·4

The specific conductivity of the solvent was $1{\cdot}1 - 2{\cdot}0 \times 10^{-6}$ at 0°, and $2{\cdot}3 - 2{\cdot}8 \times 10^{-6}$ at 25°.

The conductivity data for solutions of potassium iodide in organic solvents reported over the period 1899–1926 have been reviewed in the light of the Debye–Hückel theory.[158] The equivalent conductivity of potassium iodide solutions in ethanol has been determined; it is concluded that, at the greatest dilution used, dissociation is incomplete. The values obtained are given in Table LXIII.[159]

TABLE LXIII. - EQUIVALENT CONDUCTIVITY OF POTASSIUM IODIDE IN ETHANOL

$t = 25°$C.

V, litres/mole	10^4 mole/l.	Λ_c
16	625	24·64
32	312·5	27·90
64	156·3	32·14
128	78·125	35·96
256	39·063	39·54
512	19·531	42·55
1024	9·765	45·26
2048	4·883	47·10
4096	2·441	47·51

The solvent was dried by refluxing over lime, and had a specific conductivity of $0{\cdot}15 \times 10^{-6}$ at 25°. Subsequent conductivity studies have, however, been made in ethanol of considerably lower specific conductivity, $0{\cdot}003 \times 10^{-6}$ at 25°, and the preparation of this solvent has been described; equivalent conductivities of potassium iodide in this are shown in Table LXIV.[160]

TABLE LXIV. - EQUIVALENT CONDUCTIVITY OF POTASSIUM IODIDE IN 'ABSOLUTE' CONDUCTIVITY ETHANOL

$t = 25°$C.

10^4c	Λ_c	10^4c	Λ_c	10^4c	Λ_c
0	50·8	3·860	46·41	10·268	44·15
1·696	48·04	6·741	45·38	13·612	43·20
2·079	47·09	7·411	45·10	14·050	42·95
3·361	46·96	8·933	44·55		

The conductivities of potassium iodide solutions in aqueous ethanol have been found to follow the Kohlrausch equation: $\Lambda_c = \Lambda_0 - Xc^{1/2}$. The change in Λ_0 is approximately proportional to the change in fluidity of the solution, up to 20 mol.-% ethanol; X in the above equation shows good agreement with the Onsager slope. Some of the experimental results are recorded in Table LXV.[161]

The variation of the equivalent conductivity with concentration in pure ethanol is recorded in Table LXVI.[161]

The equivalent conductivities of potassium iodide solutions in methanol and in acetone at various temperatures have been measured with the results shown in Table LXVII.[162]

A comparison of the equivalent conductivities of potassium iodide solutions in ethanol at different temperatures is made in Table LXVIII.[163]

The following ionic mobilities have been determined:-

$\lambda^0_{K^+}$ 20·85 ($t = 25°$), 13·53 ($t = 4°$)
$\lambda^0_{I^-}$ 28·80 ($t = 25°$), 19·30 ($t = 4°$)

TABLE LXV. - ELECTRICAL CONDUCTIVITY DATA FOR SOME SOLUTIONS OF POTASSIUM IODIDE IN AQUEOUS ETHANOL

$t = 25°C.$

Mol.-% EtOH	$10^6\kappa, r^{-1}$	X	Λ_0	η c.g.s. units
0	1·086	100	151·05	0·00891
2·92	0·55	101	123·73	0·01190
6·83	0·33	57	93·67	0·01582
22·70	0·292	43	55·05	0·02309
44·63	0·192	72	48·12	0·02098
75·50	0·119	134	49·15	0·01490
100	0·065	210	50·72	0·01101

TABLE LXVI. - EQUIVALENT CONDUCTIVITY OF POTASSIUM IODIDE IN ETHANOL

$t = 25°C.$

$10^2c^{1/2}$	Λ_c	$10^2c^{1/2}$	Λ_c
1·122	149·9	3·815	147·4
1·608	149·4	4·700	146·3
2·447	148·6	5·420	145·5

The extrapolated value of Λ_0 was 151·05

TABLE LXVII. - EQUIVALENT CONDUCTIVITY OF POTASSIUM IODIDE IN METHANOL AND IN ACETONE

G. KI/l. MeOH	25°	70°	110°	140°	185°	218°
0·494	51·9	85·2	115·1	134·5	151·4	140·6
0·2077	62·2	100·1	134·5	153·6	157·0	127·6
0·01969	87·1	142·8	198·9	230·8	242·2	160·3
0·00197	105·2	178·1	260	329	395	314
G. KI/l. acetone						
0·01478	105·2	120·8	116·1	99·0	–	–
0·00034	176·9	237	279	299	240	150

TABLE LXVIII. - EQUIVALENT CONDUCTIVITIES OF POTASSIUM IODIDE SOLUTIONS IN ETHANOL AT VARIOUS TEMPERATURES

$t = 4°$, $10^6\kappa = 0·007$		$t = 15°$, $10^6\kappa = 0·0072$		$t = 25°$, $10^6\kappa = 0·0085$	
10^4c	Λ_c	10^4c	Λ_c	10^4c	Λ_c
0	32·83	0	41·03	0	49·65
0·9873	31·79	0·9818	39·64	0·6525	47·99
2·3186	31·25	2·4599	38·85	1·5363	47·51
4·4984	30·33	4·2764	38·06	2·5849	46·79
6·3003	30·08	6·1868	37·37	4·4740	45·87
8·6010	29·56	8·4013	36·73	6·1126	45·02
12·6080	28·85	12·2581	35·78	8·2691	44·18
				11·8163	43·05

κ is the specific conductivity of the solvent

The heat of solvation of potassium iodide in ethanol is +5·45 kg.-cal./mole in the temperature range 4°–15° C., and +3·9 kg.-cal./mole in the range 15°–25° C.[163] The conductivity of potassium iodide in normal and *iso*propyl alcohols is recorded in Table LXIX,[164] together with the dissociation constants in these solvents as calculated from Ostwald's dilution law and by the method of Fuoss and Kraus.[165]

TABLE LXIX. - EQUIVALENT CONDUCTIVITY AND DISSOCIATION CONSTANT OF POTASSIUM IODIDE IN *n*-PROPYL AND *iso*-PROPYL ALCOHOLS AT 25°

$10^4 \times$ Molarity	Λ_c	10^3K(Ostwald)	10^3K(Fuoss and Kraus)
n-Propyl alcohol			
0	25·42	-	-
2·842	22·39	1·998	3·950
5·202	21·19	-	-
8·429	20·12	-	-
12·260	19·07	2·890	4·229
iso-Propyl alcohol			
0	23·64	-	-
2·478	19·61	-	-
3·407	18·77	-	-
7·522	16·55	1·274	1·441
9·732	15·71	1·323	1·539

At 20° the equivalent conductivity of potassium iodide in methanol at infinite dilution, Λ_0, is 110·5. The experimental $\Lambda/c^{\frac{1}{2}}$ slope is 218 as against the Onsager slope of 231; from this the 'effective' dielectric constant of methanol at 20° is calculated to be 35·9.[166]

The equivalent conductivities of more concentrated solutions of potassium iodide in methanol at various temperatures are given in Table LXX.[167]

TABLE LXX. - EQUIVALENT CONDUCTIVITIES OF CONCENTRATED SOLUTIONS OF POTASSIUM IODIDE IN METHANOL

t°C.	Molarity = 0·2	0·4	0·6
0	45·8	39·6	35·8
10	52·5	45·5	41·4
20	59·2	51·7	47·4
30	66·8	58·7	53·3
40	73·5	65·3	59·5

The limiting equivalent conductivity, Λ_0, = 114·5 at 24°. A comparison of equivalent conductivities for this solute in water and in methanol, at 25°, and the resulting ionic mobilities, are shown in Table LXXI.[168]

TABLE LXXI. - EQUIVALENT CONDUCTIVITIES OF AQUEOUS AND METHANOL SOLUTIONS OF POTASSIUM IODIDE AT 25°

$10^4 \times$ Molarity	Λwater	ΛMeOH	$10^4 \times$ Molarity	Λwater	ΛMeOH
0	150·47	115·15	20	146·48	103·74
1	-	112·52	30	-	101·50
2	-	111·43	50	144·38	98·16
5	148·42	109·29	λ_0K^+ =	73·50	52·40
10	147·60	106·94	λ_0I^- =	76·97	62·75

The conductivity of potassium iodide solutions in acetone, and the ionic mobilities, are given in Table LXXII[169] and LXXIII.

TABLE LXXII. - EQUIVALENT CONDUCTIVITY OF POTASSIUM IODIDE SOLUTIONS IN ACETONE AT 25°C.

$10^5 \times$ Molarity	Λ_c	$10^5 \times$ Molarity	Λ_c
0	185·6	43·76	165·3
2·303	181·1	59·24	162·0
4·398	179·3	62·77	160·9
16·91	173·3	80·26	158·0
22·92	171·2	120·9	152·5
41·79	165·9	133·6	150·9

TABLE LXXIII. - LIMITING IONIC MOBILITIES FOR POTASSIUM IODIDE IN VARIOUS ORGANIC SOLVENTS AT 25°C.

	Acetone	Ethanol	Methanol	Water
$\lambda_0 K^+ =$	69·7	24·6	53·5	74·8
$\lambda_0 I^- =$	115·9	26·3	67	76·7

The following are the limiting equivalent conductivities for this system at different temperatures:-[169]

$t^\circ =$	0	25	50
$\Lambda_0 =$	147·8	185·6	229·2

The Wien effect (increased conductivity due to high field-strength) for potassium iodide in acetone is shown in Fig. 9,[170] where the field strength is represented by the spark gap of the generator in mm. The purification of acetone for conductimetric studies and the physical properties of the solvent have been studied. In this solvent, the limiting equivalent conductivity of potassium iodide was 192·8 $\text{ohm}^{-1}\text{cm.}^{-1}$ at 25°; the limiting mobility of the cation was 80·5.[171] Equivalent conductivities of potassium iodide in such 'grade I' acetone are recorded in Table LXXIV.[171a]

TABLE LXXIV. - EQUIVALENT CONDUCTIVITY OF POTASSIUM IODIDE SOLUTIONS IN ACETONE AT 25°C.

$10^7\kappa_{\text{solvent}}$	$10^4 \times$ Molarity	Λ	$10^7\kappa_{\text{solvent}}$	$10^4 \times$ Molarity	Λ
–	0	196·6*	0·236	4·317	176·4
0·236	0·8704	188·8	0·236	6·495	171·1
0·209	1·007	186·9	0·210	6·950	169·8
0·213	1·055	187·7	0·236	8·555	166·6
0·210	1·953	183·3	0·210	9·189	165·6
0·236	2·675	181·7	0·236	10·186	162·9
0·210	4·124	176·6	0·236	15·370	156·7

* After Fuoss.[165]
(Density of acetone, $d_4^{25} = 0{\cdot}7840 \pm 0{\cdot}0001$.)

From the above results, the following Stokes radii have been derived: $r_{K^+} = 3{\cdot}27$A.; $r_{I^-} = 2{\cdot}36$A.

The equivalent conductivity of potassium iodide solutions in methyl ethyl ketone has been shown to follow the relationship $\Lambda_0 = \Lambda_c + a.c^{\frac{1}{2}}$; Λ_0 at 25° = 148, a = 1352. Limiting ionic mobilities (λ) and solvation numbers (S) in some organic solvents are as shown on the following page.[172]

The results of conductivity measurements on solutions of potassium iodide in nitromethane are given in Tables LXXV and LXXVI.

	Methyl alcohol	Ethyl alcohol	Acetone	Methyl ethyl ketone	Acetonitrile
λ_{K^+}	53·5	24·5	69·6	65·0	85·9
λ_{I^-}	61·0	26·4	116·0	82·3	101·0
S_{K^+}	4	3–4	4	2	3
S_{I^-}	1	2	0–1	0–1	0–1

TABLE LXXV. - EQUIVALENT CONDUCTIVITY, AND FLUIDITY, OF POTASSIUM IODIDE IN NITROMETHANE[173]

	0°	25°	40°	55°	70°	85°
Λ_0	90·2	121·8*	143·0	164·8	191·1	213·4
Λ (c = 0·01)	67·2	88·1	101·7	114·5	127·3	140·3
Λ (c = 0·008)	83·1	111·6	130·6	150·0	170·7	191·4
Fluidity of solvent	118·6	158·3	190·0	222·2	254·8	291·8

(* A later value,[174] 122, is in rather better agreement than the result in Table LXXVI.)

TABLE LXXVI. - EQUIVALENT CONDUCTIVITY OF POTASSIUM IODIDE IN NITROMETHANE AT 25° C.[175]

10^5 × Molarity	Λ	10^5 × Molarity	Λ
0	121·2	62·05	113·8
10·91	118·1	92·00	111·9
21·01	116·9	114·8	110·8
43·27	114·8	283·6	104·9

These results may be represented by the equation:-

$$\Lambda = 121{\cdot}2 - 304c^{1/2}$$

The constants listed below apply to the equation:-

$$\Lambda_c = \Lambda_0 - a.c^{1/2},$$

for potassium iodide in some organic solvents at 25°.

Ethyl cyanoacetate: $\Lambda_0 = 25{\cdot}01$, $a = 115{\cdot}2$ (Ref. 176)
o-Toluonitrile: $\Lambda_0 = 41{\cdot}08$, $a = 253{\cdot}3$ (Ref. 176)
Benzonitrile: $\Lambda_0 = 52{\cdot}12$, $a = 263{\cdot}3$ (Ref. 177)

In the last solvent the mean ionic radius is $\bar{r}_{KI} = 2{\cdot}57$A., and the ionic mobilities are $\lambda^0_{K^+} = 22{\cdot}6$, $\lambda^0_{I^-} = 29{\cdot}5$.[177]

The following are the molar conductivities at 18° for potassium iodide in epichlorhydrin (boiling point 115°):-[178]

V, litres/mole	60	120	240	480
μ, ohm^{-1}	13·8	15·6	19·2	25·4

Conductivities in acetophenone are recorded in Table LXXVII.[179]

Conductivity data for potassium iodide in ethylenediamine solution are shown in Table LXXVIII.[180]

The following are the molar conductivities of potassium iodide in fused acetamide at 90°:-[181]

V, litres/g.-equiv.	10	40	160	320	960	∞
μ	30·4	33·8	38·0	39·1	40·5	43

The solvent had the specific conductivity $1{\cdot}5 \times 10^{-5}$ ohm^{-1} at 90°.

TABLE LXXVII. - CONDUCTIVITY OF POTASSIUM IODIDE SOLUTIONS IN ACETOPHENONE AT CONCENTRATION c (IN G.-FORMULA WT. PER LITRE IN VACUO)

10^5c	$10^6\kappa$, ohm^{-1}	Λ	10^5c	$10^6\kappa$, ohm^{-1}	Λ
0·3398	0·1352	39·79	103·0	33·90	32·91
0·7924	0·3072	38·76	182·1	52·47	28·81
1·621	0·6276	38·73	295·1	78·67	26·66
4·143	1·577	38·06	300·9	85·12	28·29
6·732	2·612	38·79	432·9	109·3	25·25
13·58	4·974	36·68	654·0	151·9	23·23
53·44	18·04	33·76	565·9	135·1	23·88

TABLE LXXVIII. - CONDUCTIVITY OF POTASSIUM IODIDE SOLUTIONS IN ETHYLENEDIAMINE AT 25°C.

$10^3 \times$ Molarity	Λ	$10^3 \times$ Molarity	Λ
4·595	27·8	0·216	53·9
3·140	31·5	0·122	58·1
1·696	37·1	0·099	60·1
0·950	41·4	0·062	62·2
0·453	48·1	0·049	65·5
0·348	50·2	0	69·2

The solvent had specific conductivity $\kappa = 9 \times 10^{-8}$ ohm^{-1} at 25°. The results are interpreted in terms of the generalized acid-base theory.

Conductivity data for solutions of potassium iodide in N-methylacetamide are reported in Table LXXIX.[182]

TABLE LXXIX. - CONDUCTIVITY DATA FOR SOLUTIONS OF POTASSIUM IODIDE IN N-METHYLACETAMIDE

$t°$	Dielectric const. solvent	Λ_0	$\Lambda_0\eta$	Expt. slope	Onsager slope	Deviation %
30	179	18·1	0·705	11·4	10·3	11
40	166	23·1	0·698	15·3	13·7	12

Data for dimethylformamide solutions of potassium iodide are given in Table LXXX.[183]

TABLE LXXX. - EQUIVALENT CONDUCTIVITY OF POTASSIUM IODIDE SOLUTIONS IN DIMETHYLFORMAMIDE AT 25°C.

10^4 Molarity	Λ	10^4 Molarity	Λ
1·237	81·1	18·48	76·7
3·616	79·9	28·51	75·3
6·542	79·0	38·37	74·3
11·71	77·8	48·87	73·4

(Onsager slope, 158; observed slope, 137. $\Lambda_0 = 82·6$ at 25°C.)

Some interesting results were given by a study of more concentrated solutions in ethylenediamine: the equivalent conductivity shows a maximum at about 0·9N, presumably as a result of solute-solvent interaction.

Further results at 15°, 50° and 80° are also given.

Conductivity studies in furfural gave the results shown in Table LXXXII.[185] The solvent had the specific conductivity 1·38 – 4·77 × 10^{-6} ohm^{-1} at 25°.

TABLE LXXXI. - EQUIVALENT CONDUCTIVITY OF CONCENTRATED SOLUTIONS OF POTASSIUM IODIDE IN ETHYLENEDIAMINE AT 25°C.[184]

Normality	Λ	Normality	Λ
0·247	16·0	1·119	18·9
0·414	17·5	1·570	17·5
0·550	18·3	1·928	16·0
0·668	18·7	2·240	14·6
0·804	18·7	2·721	12·09
0·830	18·9	3·050	10·99
0·941	19·0		

TABLE LXXXII. - EQUIVALENT CONDUCTIVITY OF POTASSIUM IODIDE SOLUTIONS IN FURFURAL AT 25°C.

Molarity	Λ	$\Lambda/\Lambda_0 = \alpha$	Molarity	Λ	$\Lambda/\Lambda_0 = \alpha$
0·1	30·50	0·708	0·005	41·43	0·961
0·05	33·81	0·784	0·002	42·20	0·979
0·02	37·60	0·872	0·001	42·40	0·984
0·01	39·99	0·928	0·0005	42·50	0·986

$\Lambda_0 = 43{\cdot}10$ at 25°

The solvation of the cation was estimated to be about 1·44, compared with 1·3 in aqueous solutions.

In the mixed solvent ethylenediamine–methanol, having $d_4^{20} = 0{\cdot}8829$, viscosity 0·0167 poise at 20° and dielectric constant, 27·2, potassium iodide was only partially dissociated; $10^3K = 1{\cdot}47$ at 20°.[186]

The distribution of potassium iodide between glycol and ethyl acetate has been measured, with the results shown in Table LXXXIII. The activity coefficient of the solute is estimated to vary from 1·02 (at 0·0694 molarity) to 1·14 (at 0·2770 molarity) in the solvent glycol, the activity coefficient of ammonium iodide in this solvent being taken to be 1·0 within this range of concentration.[187]

TABLE LXXXIII. - DISTRIBUTION OF POTASSIUM IODIDE BETWEEN GLYCOL AND ETHYL ACETATE

Moles/l. KI in glycol, = a	Moles/l. KI in EtOAc, = b	a/b
0·0694	0·0358	194
0·1511	0·0822	184
0·1870	0·1020	183
0·2123	0·1172	182
0·2770	0·1590	174

The zeta-potential and its variation with concentration for potassium iodide solutions in a number of alcohols has been measured: the results are shown in Fig. 10.[188]

The conductivity of solutions of potassium iodide in methanol is slightly decreased by adding small amounts of iodine and increased by the addition of larger amounts. The results are shown in Table LXXXIV. Increase in conductivity cannot be due to increased ionic mobility, for iodine increases the viscosity of these solutions; an explanation is given in terms of the dissociation of associated complexes in the solution.[189]

In acetone solutions, addition of iodine produces an increase in conductivity at all temperatures considered, as shown in Fig. 11.[189]

TABLE LXXXIV. - SPECIFIC CONDUCTIVITY OF SOLUTIONS OF POTASSIUM IODIDE IN METHANOL CONTAINING ADDED IODINE

Wt.-% iodine	5·071 Wt.-% KI soln.			
	t°	$10^3\kappa$	t°	$10^3\kappa$
0	33	16	9	12
0·0362	20	14	8·5	12
0·518	30	16	7	12
2·384	10	13	37	18
9·435	40	20	11	14

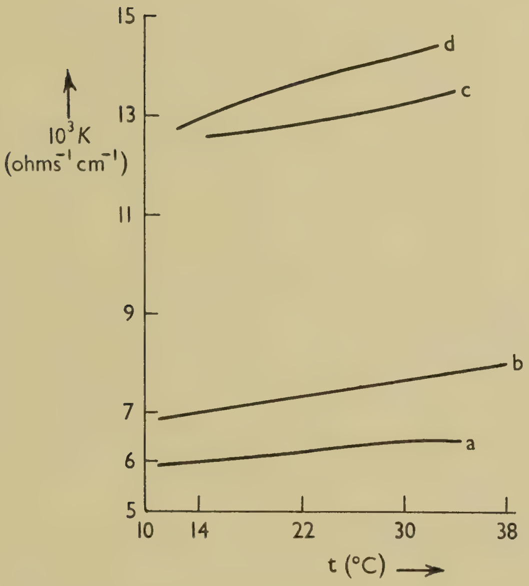


FIG. 11. THE EFFECT OF ADDED IODINE ON THE CONDUCTIVITY OF POTASSIUM IODIDE (1·602%) IN ACETONE AT TEMPERATURES BETWEEN 10° AND 40°C.

a. No I_2 c. 5·384% I_2
b. 1·147% I_2 d. 5·384% I_2 - after 12 hours standing

Chemical Properties

The influence of water vapour on the reaction between potassium iodide and chlorine has been studied.[190] For appreciable reaction to occur, a minimum partial pressure of water vapour approximating to the vapour pressure of the saturated solution at the temperature of reaction must be attained.

Potassium iodide reacts with hydrogen peroxide in acid solution to give iodine; a spectrographic study of the reaction supports the mechanism: $2I^- + H_2O_2 + 2H^+ \rightarrow I_2 + 2H_2O$ at higher reactant concentrations.[191] In alkaline solution the interaction of potassium iodide with hydrogen peroxide first produces the hypoiodite, KIO, which is subsequently reduced by the peroxide. The oxidation of potassium iodide to potassium iodate in alkaline solution requires a stronger oxidizing agent such as ozone.[192] This catalytic decomposition of hydrogen peroxide by potassium iodide in alkaline solution may be advantageously applied in the iodometric determination of chromium; after oxidation to chromate, the alkaline solution is boiled with 1g. of potassium iodide to decompose excess peroxide.[193]

The rate of decomposition of hydrogen peroxide by potassium iodide has been measured in various solvents.[194] The following are results in water at 25°:-

Catalyst (KI) concn.	0·01N.	0·02N.	0·04N.
$k_{25°}$, sec.$^{-1}$	0·01347	0·02691	0·05428

The ratio (rate at $t + 10°$)/(rate at $t°$) = 2·114, and the activation energy is 13·64 kg.-cal./mole. At unit catalyst concentration, $k_{25°}$(mean) = 1·350 sec.$^{-1}$ The reaction in water, methanol and probably in glycol, involves a triple collision; e.g. $H_2O_2 + H_2O + I^-$ in water. On this assumption the rate equation of Jowett[195] gives good agreement between calculated and observed rates. In absolute ethanol, the solvent does not appear to participate in the rate-determining step; the bimolecular collision ($I^- + H_2O_2$) and the activation energy, 15·53 kg.-cal./mole, account satisfactorily for the observed rate.

The oxidation of potassium iodide solution by hydrogen peroxide in the presence of ferrous salts has been investigated; the formation of a peroxide of iron in these solutions is postulated.[196] Ferric hydroxide may replace ferrous salts in this oxidation; its activity is associated with the active OH groups present.[197]

The oxidation of potassium iodide solution by oxygen, in an electric glow discharge, has been studied; the activation energy is very small, less than 1 kg.-cal./mole.[198] Passage of oxygen and simultaneous irradiation with light of short wave-length (down to 253mμ) gave about 5% liberation of iodine.[199]

Oxidation of potassium iodide solution by ozone is increased by dilution of the gas (originally 2–7mg.O_3/litre) with air.[200] The overall equation, $2I^- + O_3 + H_2O \rightarrow O_2 + I_2 + 2OH^-$, for the reaction in a buffered solution at pH 7 is the result of two simultaneous reactions, one forming iodate, $I^- + 3O_3 \rightarrow IO_3^- + 3O_2$, the other forming iodine. Iodate formation decreases as the ozone concentration falls.[201-203]

A photoelectric colorimeter has been described, and used to follow the oxidation of potassium iodide by hydrogen peroxide in presence of ferrous ions. The concentration of potassium iodide was 0·015 mole/litre,[204] and graphs are given showing the variation in reaction rate with:-

(1) variation of catalyst concentration from 2×10^{-6} to 10^{-4} mole/litre, in dilute sulphuric acid and in neutral solution.

(2) variation of hydrogen peroxide concentration from $2{\cdot}8 \times 10^{-5}$ to $2{\cdot}8 \times 10^{-4}$ mole/litre at a fixed ferrous sulphate concentration of 4×10^{-4} mole/litre in dilute sulphuric acid.

The oxidation of potassium iodide solutions by complex cobaltammines shows maximum reaction at pH 6, and is essentially catalytic.[205]

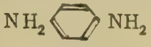
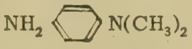
The reaction between potassium iodide and sulphur trioxide proceeds according to the equation:-

$$2KI + 4SO_3 \rightarrow K_2S_3O_{10} + I_2 + SO_2.$$

X-Ray analysis shows no trace of $K_2S_2O_7$ though this is formed in the analogous oxidation of potassium fluoride or chloride.[206] In the reaction of potassium iodide and potassium peroxydisulphate, $K_2S_2O_8$, sodium salts added alone show only a kinetic salt effect but in the presence of cupric ions they act as catalyst promoters.[207]

In the absence of a catalyst, the reaction of potassium iodide and persulphates is between molecules rather than ions: the effectiveness of some organic catalysts at concentrations of 10^{-3} mole/l. is shown in Table LXXXV.[208]

TABLE LXXXV. - CATALYSIS OF THE POTASSIUM IODIDE-PERSULPHATE REACTION BY ORGANIC AMINES

KI = 0·1 mole/l.	
Catalyst	% Acceleration
$NH_2.NH_2$	13·5
$NH_2(CH_2)_2NH_2$	15
$NH_2(CH_2)_5NH_2$	22·6
	102
	182
Aniline hydrochloride	14
Dimethylaniline	13
Diphenylamine	8
Aminoazobenzene	11
p-Aminophenol	13
Benzidine	2

These reactions are ionic; two amino groups separated by an optimum distance show the greatest catalytic activity.

The reaction between potassium iodide and potassium perdisulphate is bimolecular in light of wave-length 4725A. to 7304A., and the quantum yield is high. At these wave-lengths the temperature coefficient is about 1·6, over the range 20° to 30°.[209] The quantum efficiency of this and similar reactions usually increases with rise in temperature.[210]

Comprehensive experimental data have been recorded for the reaction of potassium iodide and potassium perdisulphate in sunlight and in light from a 1000-watt lamp. The reaction velocity is proportional to the square root of the incident light intensity:[211] zinc oxide sensitized the reaction.[212] The quantum efficiency for this reaction at various wave-lengths is found to be low.[213] The interaction of 0·2M. potassium iodide solution and 0·1M. ammonium perdisulphate is bimolecular and affords a convenient study of the effect of concentration upon reaction rate.[214]

The formation of potassium iodate, by melting potassium iodide with potassium bromate, chlorate or perchlorate, has been studied. The results are summarized below:-[215]

ratio $KI{:}KBrO_3$ = 2:1 yield KIO_3 = 81·3% theory
1:1 yield KIO_3 = 69·4%
$KI{:}KClO_3$ = 2:1 yield KIO_3 = 62·0%
1:1 yield KIO_3 = 41·7%
$KI{:}KClO_4$ = 2:1 yield KIO_3 = 71·9%
4:3 yield KIO_3 = 57·5%

The reaction $2KBrO_3 + I_2 \rightleftharpoons 2KIO_3 + Br_2$, which takes place without a catalyst, is followed in the presence of potassium iodide by the further stage, $2KI + Br_2 \rightleftharpoons 2KBr + I_2$. With potassium chlorate reaction is less complete.[216]

The following mechanism is proposed for the thermal decomposition of potassium iodide in the presence of sodium metaphosphate:-

$$2KI + Na_2P_2O_6 + \tfrac{1}{2}O_2 \rightarrow Na_2K_2P_2O_7 + I_2$$
$$2KI + Na_2K_2P_2O_7 + \tfrac{1}{2}O_2 \rightarrow 2NaK_2PO_4 + I_2$$
$$2NaK_2PO_4 + Na_2P_2O_6 \rightarrow 2Na_2K_2P_2O_7$$

The rate of reaction in the temperature range 200°–900° depends upon the surface area:volume ratio and on the material of the reaction vessel.[217]

The kinetics of the interaction of potassium iodide and ferric ions have been studied; the overall reaction is:-

$$FeCl_3 + KI \rightarrow FeCl_2 + KCl + I,$$

and there is no photochemical reaction in the absence of free iodine.[218] Conductivity measurements demonstrate the presence of the ions $FeCl_2^+$, $FeICl^+$, FeI_2^+, $FeCl^{++}$ and FeI^{++} and a rate equation is proposed.[219]

The oxidation of arsenious acid by ferric chloride is catalyzed by potassium iodide; the iodide ion is first oxidized by Fe^{+++} to iodine, which then oxidizes the acid.[220]

The equilibrium: $2Fe(CN)_6^{3-} + 3I^- \rightleftharpoons 2Fe(CN)_6^{4-} + I_3^-$ has been studied for the potassium salts in aqueous solution and in potassium chloride solution.[221] Allowing for salt effects, $K_{eq.} = 10^{-3}$, and is unaltered by reducing the pH to 3·5.

The reaction between potassium iodide and potassium dichromate, $2K_2Cr_2O_7 + 2KI \rightarrow 3K_2CrO_4 + CrO_2 + 2I$, is first-order between equimolar weights of the reactants.[222] In acid solution, the reaction is:-

$$3H_2Cr_2O_7 + 4KI \rightarrow 2K_2Cr_2O_7 + 2CrO_2 + 3H_2O + 4I.$$

The velocity of the reaction is at every instant proportional to the pH;[223] this is also true in 'neutral' dichromate, owing to the hydrolysis, $2K_2Cr_2O_7 + H_2O \rightleftharpoons 2K_2CrO_4 + H_2Cr_2O_7$.[222]

The reduction of potassium dichromate by iodide ions has been studied potentiometrically; with potassium iodide the formation of iodine monochloride, ICl, was detected, and this re-forms chloride ions on further addition of potassium iodide.[224]

The action of nitrous acid on aqueous potassium iodide solutions may be represented:[225] $2HNO_2 + KI \rightarrow KNO_2 + NO + \frac{1}{2}I_2 + H_2O$. The reaction between sodium nitrite and potassium iodide in aqueous acetic acid is unimolecular with respect to each reactant and the velocity is proportional to the hydrogen ion concentration; alkali metal chlorides, nitrates and sulphates accelerate the reaction.[226]

The reactions of potassium iodide with dinitrogen tetroxide have been studied.[227-229] The basic reactions are:-

$$\begin{array}{ll} (1)\ N_2O_4 + 2KI & \rightarrow 2KNO_2 + I_2 \\ (2)\ N_2O_4 + H_2O & \rightarrow HNO_2 + HNO_3 \\ (3)\ KI + HNO_2 & \rightarrow NO + KOH + \frac{1}{2}I_2 \\ (4)\ HNO_3 + KOH & \rightarrow KNO_3 + H_2O \end{array}$$

Nitric oxide reacts to some extent with dinitrogen tetroxide forming N_2O_3 when absorption is rapid; when it is slow reaction (2) predominates. If N_2O_3 is formed it reacts with water to form nitrous acid, and nitric oxide is re-formed according to reaction (5):-

$$(5)\ 4HNO_2 + 2KI \rightarrow 2KNO_2 + 2NO + I_2 + 2H_2O.$$

Thus nitrite is formed in reactions (1) and (5), the former becoming less important with increasing dilution. In alkaline solution nitric oxide is evolved from this system, and this affects the quantitative determination of dinitrogen tetroxide by means of potassium iodide.

A spectrophotometric investigation of the interaction of potassium iodide and osmium tetroxide has shown that for concentrations of potassium iodide less than 2% by weight, the mixture is yellow in colour and its aqueous solution is stable. It is suggested that a complex, $K(OsO_4I.H_2O)$, is formed.

When the concentration is greater than 2%, the I_3^- ion is present.[230]

In 2N. hydrochloric acid solution potassium iodide reacts quantitatively with sulphur monochloride (S_2Cl_2) with the liberation of iodine. Trichloromethylsulphenyl chloride, Cl_3CSCl, reacts similarly, the number of chlorine atoms taking part varying from 2·4 to 3·1, as shown by titrating the liberated iodine with thiosulphate.[231]

Potassium iodide is oxidized by hydrogen peroxide and methyl, ethyl and *tert.*-butyl hydroperoxide. The reactions are first-order with regard to peroxide at constant iodide concentration; for the ethyl hydroperoxide reaction, the activation energy is 12·7 kg.-cal./mole.[232]

The reaction between potassium iodide and bismuth tri-iodide in acetone has been investigated colorimetrically. It is concluded that a complex salt, KI,BI_3, is formed, with dissociation constant $K_{20} = 2 \times 10^{-6}$. Similar results were obtained in methanol, ethanol and benzonitrile as solvents.[233]

On gelatin and agar, the periodic reaction:-

$$Pb(NO_3)_2 + 2KI \rightarrow PbI_2 + 2KNO_3,$$

has been studied. The product of diffusion velocity and distance between rings was found to be approximately constant.[234,235]

The chromates of silver and of monovalent mercury and thallium react with potassium iodide to form the insoluble iodides; mercuric chromate and bismuth chromate react further to form double iodides. Barium and lead chromates do not react with potassium iodide.[236]

The reaction between organic halides and potassium iodide in acetone may be followed conductimetrically where the potassium halide is insoluble in that solvent.[237] Some rate constants determined at 20° by this method are compared with those established volumetrically;[238] thus, reactions of substituted benzyl chlorides in acetone with potassium iodide at 20° have the following rate constants:-

Substituent	k_{20°(volumetric)	k_{20°(conductimetric)
p-chloro-	2·80	2·89
o-nitro-	11·4	12·1

A study of the inhibitive effect of potassium iodide on the rate of solution of carbon steel in nitric acid has shown that the cathodic process is affected.[239]

The corrosion of lead by solutions of potassium iodide has been studied: at 20° corrosion is very slow for concentrations of potassium iodide up to 0·1N., but rapid in 2N. solutions. At the higher concentrations, the film of corrosion products is found to contain $KPbI_3$. At 20°, the relative corrosive effects of some potassium salts were in the order:-[240]

$$<0{\cdot}05\text{N. soln., } KNO_3 > KCl > KBr = K_2SO_4 > KI$$
$$>0{\cdot}05\text{N. soln., } KI = KNO_3 > KCl > KBr = K_2SO_4$$

The role of potassium iodide in the colour reaction between iodine and starch has been investigated. From a 0·5% starch suspension, a blue-black precipitate was obtained with excess iodine in 0·1N. potassium iodide; this had the composition $(((C_6H_{10}O_5)4I)_4,KI)_n$[241,242] (see also Mellor,Suppl. 2,Pt. 1,842).

Oxidation of aqueous solutions of potassium iodide by α-particles and *X*-rays has been studied;[243] the extent of the oxidation by *X*-rays increases with temperature and decreases with increasing wave-length of the radiation.[244] For decomposition by slow electrons, there appears to be a correlation between the heat of formation and the decomposition threshold voltage with potassium chloride but not with potassium iodide; the lack of correlation is more marked for salts of divalent cations, such as barium chloride, and the correspondence mentioned above is considered to be fortuitous.[245]

The equilibrium distribution of sodium and potassium from their amalgams and solutions of sodium and potassium iodides has been studied.[246] Defining the equilibrium constant as $K = \frac{[K/Hg][NaI]}{[Na/Hg][KI]}$ it was found that:-

(i) at fixed total salt concentration, K decreases with increasing amalgam concentration;

(ii) at fixed amalgam and total salt concentrations, K remains constant in spite of variations in the salt ratio;

(iii) at fixed amalgam concentration, K decreases with increasing concentration of the mixed salt solution.

The equilibrium between sodium and fused potassium iodide has been investigated at a temperature of 800° C. The value for the equilibrium constant, given as $\frac{[Na][KI]}{[K][NaI]}$, is 56.[247]

Sixty reciprocal pairs of alkali halides were examined by fusing at a suitable temperature, quenching the resultant mixture and examining it by X-ray analysis.[248] In almost every case it was found that the heavy cation was linked to the heavy anion and *vice versa.* The two binary salts so formed are referred to as the 'stable pair'. A reaction has been observed at a temperature as low as 100° C. below the fusion temperature after heating for 36 hours. On heating the stable pairs (in which lithium was not included) to a temperature 100° below fusion point, it was shown that no reversion to the reciprocal pair occurred. On the other hand, heating the reciprocal pairs always brought about at least partial conversion to the stable pairs. Of pairs which included lithium halides, some of the stable pairs underwent partial reversion to the reciprocal pairs at certain temperatures. For example, the stable pair lithium chloride–sodium iodide is partially converted at 400°, but no conversion occurs at this temperature for the stable pair lithium chloride–potassium iodide. Caesium chloride and potassium bromide reach an equilibrium under all conditions. When lithium and fluoride were included in the system, lithium fluoride was always found in the stable pair. Very little reaction occurred at temperatures 200° below fusion point.

A method for the estimation of equilibrium constants in reciprocal salt pair systems which has been proposed, is based on the fact that the temperature change on mixing the components of the system is a minimum when the components are taken in their equilibrium concentrations and a maximum for a mixture of the reactants alone.[249] Some of the results obtained are shown in Table LXXXVI.

TABLE LXXXVI.- THE EQUILIBRIUM CONSTANTS FOR SOME RECIPROCAL PAIRS OF ALKALI HALIDES

Reciprocal pair	Temperature (°C.)	Equilibrium constant
KI–NaCl	777	1·62
KI–NaBr	777	10·02
KBr–NaCl	769	1·75

From an extensive survey of binary systems the following rule has been deduced: if components A and B have a liquidus which is approximately linear with respect to composition in mol.-%, then the liquidus for systems A–C and B–C, where C is a third component, will also be linear. This is demonstrated for the systems KI–K_2SO_4 and KBr-K_2SO_4.[250]

Potassium iodide undergoes homeomorphic transformation from the α to the β phase at 11°C.[251]

The system potassium iodide–ammonium iodide has been studied by thermal analysis in the temperature range −100° to 20° C.; the well-known NH_4I transition at −42° persists in this system up to 55 mol.-% KI. The first-order transition of pure ammonium iodide at −7° appears also in a solid solution with potassium iodide, but between −10° and −13° up to 4 mol.-% KI.[252]

The binary system potassium iodide–lead iodide has been investigated; the phase diagram is shown in Fig. 12. Binary eutectics are observed at 321° (31 mol.-% KI) and at 346° (52·5 mol.-% KI). The maximum at 349° and 50 mol.-% KI is the congruent melting-point of the compound $KPbI_3$.[253]

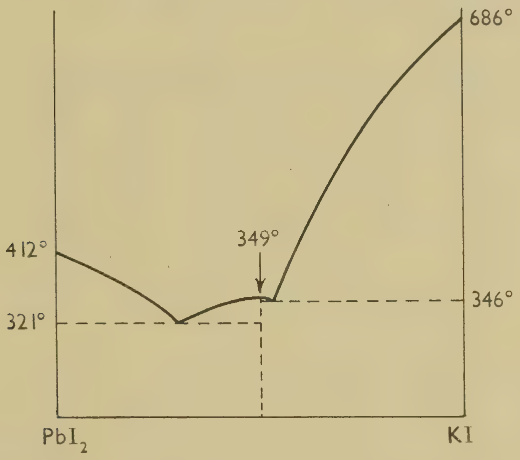


FIG. 12. THE BINARY SYSTEM $KI–PbI_2$

A study of the vapour pressure of solutions of potassium iodide in liquid sulphur dioxide shows the compound $KI,2SO_2$ to be present at 0° to −10°.[254,255] Electrolysis of the above solution probably first leads to liberation of potassium at the cathode, which reacts with sulphur dioxide to form successively the hyposulphite, thiosulphate and pyrosulphite.[256] No free sulphur is formed over the temperature range −18° to −21°.

Solubility, viscosity and specific gravity studies on the ternary system potassium iodide–potassium bromide–water, at 0°, 15°, 35° and 50° show two fields of limited solid solution, meeting at a point where the viscosity and specific gravity isotherms also break sharply. In Table LXXXVII are listed the specific gravity, viscosity and composition at this point of intersection, for the experimental temperatures.[257]

TABLE LXXXVII. - DATA FOR THE SYSTEM POTASSIUM BROMIDE–POTASSIUM IODIDE–WATER, AT THE POINT OF INTERSECTION OF THE SOLID SOLUTIONS

t°	Sp. gravity	Viscosity c.g.s. units	Wt.-%	
			KBr	KI
0	1·6596	1·5197	6·95	83·57
15	1·6980	1·1984	9·47	83·03
35	1·7442	1·0606	49·25	34·70
50	1·7628	1·0030	40·60	57·14

The system potassium iodide–sodium iodide–water shows no compound formation at 8°, 25° and 40°. A hydrate of sodium iodide, $NaI,2H_2O$, is formed, but the potassium salt remains anhydrous.[258]

In the ternary system potassium fluoride–potassium iodide–water the solid phase separating from saturated solution over the complete range of composition is a solid solution of variable composition. The method used was to measure the change in electrical conductivity upon adding a third component to a solution of the other two; this, however, yields no information as to the composition of the solid phase. Some saturated solution compositions are listed in Table LXXXVIII.[259]

TABLE LXXXVIII. - COMPOSITION OF SATURATED SOLUTIONS IN THE SYSTEM POTASSIUM FLUORIDE–POTASSIUM IODIDE–WATER AT 25°C.

H_2O	KI	KF	H_2O	KI	KF
86·08	13·92	0	84·97	6·22	8·81
86·08	12·58	1·34	84·28	5·19	10·53
85·58	10·08	4·34	83·97	3·78	12·25
85·87	9·44	4·69	82·48	2·22	15·30
85·82	9·42	4·74	79·82	1·21	18·97
85·41	7·49	7·10	76·03	0	23·92

An example of the change in slope of the conductivity–concentration curve, at the point of separation of a solid phase, is illustrated in Table LXXXIX.

TABLE LXXXIX. - SPECIFIC CONDUCTIVITY OF MIXTURES IN THE SYSTEM POTASSIUM FLUORIDE–POTASSIUM IODIDE–WATER AT 25°C.

Composition, mole %			κ, ohm^{-1}
H_2O	KF	KI	
83·91	15·57	0·52	0·3060
83·62	15·51	0·87	0·3086
83·33	15·46	1·21	0·3112
83·05	15·40	1·55	0·3136
82·49	15·30	2·21	0·3210
82·20	15·43	2·37*	0·3125
81·37	15·10	3·53	0·3048
80·56	14·95	4·49	0·2987
80·05	14·82	5·13	0·2833

* Point of separation of solid phase

The following solid phases have been isolated from the system potassium iodide–cadmium iodide–water:

$CdI_2,2KI,2H_2O$; recrystallized from water between 76° and 81·4°.
$CdI_2,2KI,3H_2O$; crystallizes below −15·3°.
$CdI_2,2KI,\frac{1}{2}H_2O$; crystallizes above 76·3°.
CdI_2,KI; was obtained by fusion and does not crystallize as such.
$2CdI_2,3KI,4H_2O$; crystallizes between 10·4° and −27·7°, but is decomposed by solutions outside a restricted composition range.[260]

The system potassium iodide–potassium sulphate–water at 25° shows no hydrates, eutectic points or double salts.[261]

The boiling point elevations of solutions of potassium iodide containing various proportions of added arsenious oxide are normal; any compounds formed must decompose below the boiling point.[262]

The reciprocal system potassium iodide–sodium iodide–potassium carbonate–sodium carbonate is illustrated in Fig. 13.[263] The binary iodide system NaI/KI forms a continuous series of solid solutions with a minimum at 574° and approximately 50% KI. The binary system KI/K_2CO_3 forms a eutectic at 612° and 60% KI.

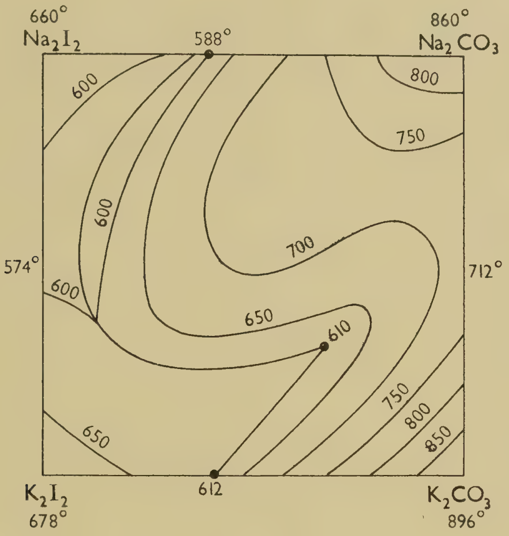


FIG. 13. THE QUATERNARY SYSTEM KI–NaI–K_2CO_3–Na_2CO_3

The binary eutectics in the system sodium iodide–potassium bromide are as follows:-

NaBr–KBr, 635°, 48% KBr
KBr–KI, 662°, 27% KBr
NaI–KI, 580°, 58% NaI
NaBr–NaI, 650°, 72% NaI[264]

This system is illustrated in Fig. 14.

The melting-point composition diagram for the ternary system potassium chloride–potassium bromide–potassium iodide is shown in Fig. 15; the binary eutectics are:-

KBr–KCl, 734°, 71% KBr
KBr–KI, 664°, 29% KBr
KCl–KI, 588°, 47% KCl[265]

The reversible reciprocal system of sodium and potassium iodides and nitrates is shown in Fig. 16;[266] the following are the singularities of this diagram:-

223°; minimum for the binary nitrate system Na/K NO_3, at 50% $NaNO_3$
580°; minimum for the binary iodide system Na/K I, at 40% KI
296°; eutectic for the system NaI/$NaNO_3$, at 87% $NaNO_3$
358°; point of inflexion of the system KI/KNO_3, at 7% KI

There is no evidence of compound formation in this system; the ternary

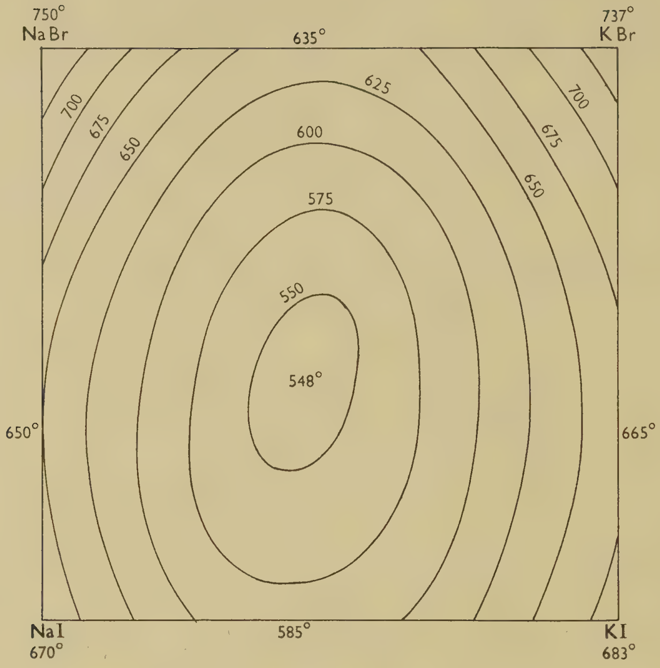


FIG. 14. THE QUATERNARY SYSTEM KI–NaI–KBr–NaBr

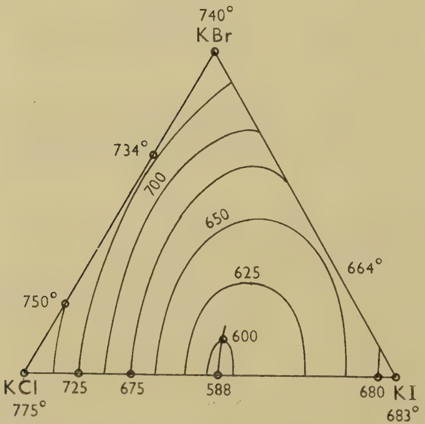


FIG. 15. THE TERNARY SYSTEM KI–KCl–KBr

eutectic at 222° has the composition 51·5% $NaNO_3$, 42% KNO_3, 6·2% KI.

In the reciprocal system potassium chloride–sodium iodide, the singular

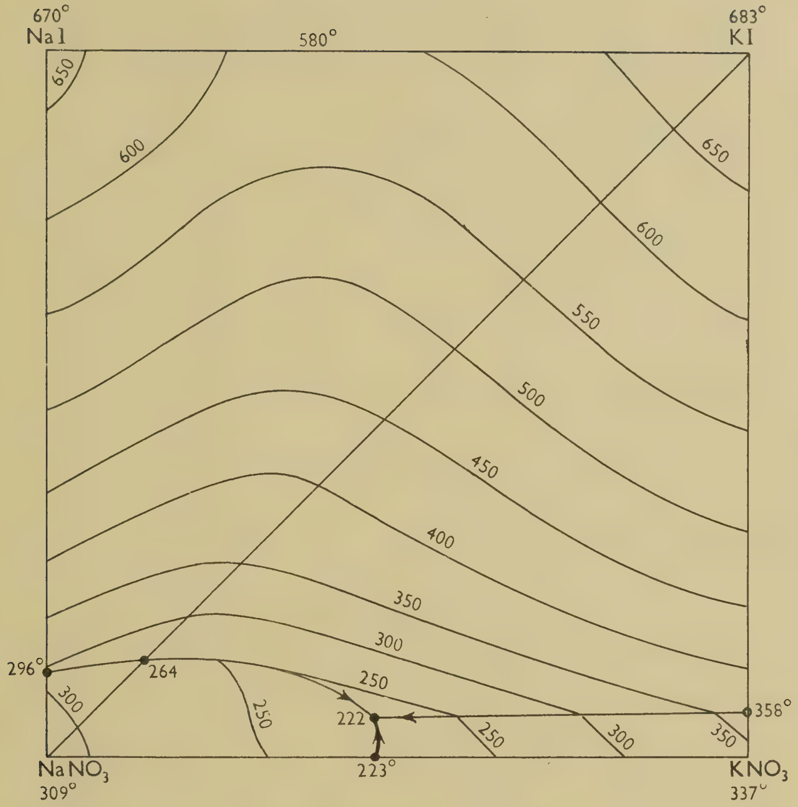


FIG. 16. THE QUATERNARY SYSTEM KI-NaI-KNO_3-$NaNO_3$

points are:-[267]

586°, minimum for the binary NaI/KI system, at 42% KI
598°, eutectic for the binary KI/KCl system, at 55% KI
514°, eutectic for the binary KI/NaCl system, at 56·5% KI

The singular mutual irreversible system potassium iodide–thallium nitrate shows the following singularities:-

203°, eutectic, of composition 95% $TlNO_3$
440°, a congruently-melting compound at 50% KI
432°, eutectic at 43·5% $TlNO_3$[268]

The irreversible reciprocal system potassium iodide–silver bromide has been studied.[269] The binary pairs AgBr–AgI and KBr–KI form continuous series of solid solutions; this is surprising in the case of the first pair, because of the reluctance of silver bromide to adopt the four-co-ordinated structure of silver iodide. Singularities within this system are as follows:-

AgBr–KBr	eutectic	285°	68 mol.-% AgBr
AgI–KI	eutectic	243°	69·5 mol.-% AgI
	unstable compound KI,4AgI decomposing at 267°		
AgBr–KI	eutectic	264°	80·3 mol.-% AgBr
AgI–KBr	eutectic	361°	84 mol.-% AgI
AgBr–50:50KBr,KI	eutectic	273°	76·4 mol.-% AgBr 11·8 mol.-% KBr 11·8 mol.-% KI
AgI–50:50KBr,KI	eutectic	336°	81·4 mol.-% AgI 9·3 mol.-% KBr 9·3 mol.-% KI
KI–70AgI,30AgBr	eutectic	360°	21·2 mol.-% AgBr 68·6 mol.-% AgI 16·2 mol.-% KI
KI–50:50AgI,AgBr	eutectic	334°	15·4 mol.-% KI 42·3 mol.-% AgI 42·3 mol.-% AgBr
KI–6AgBr,94AgI	eutectic	283°	24·5 mol.-% KI 71 mol.-% AgI 4·5 mol.-% AgBr
	transition point	285°	21·5 mol.-% KI 73·8 mol.-% AgI 4·7 mol.-% AgBr
KI–7·5AgBr,92·5AgI	eutectic	300°	20·4 mol.-% KI 73·6 mol.-% AgI 6 mol.-% AgBr
	transition point	298°	21·3 mol.-% KI 72·4 mol.-% AgI 5·9 mol.-% AgBr
KI–87·5AgBr,12·5AgI	eutectic	253°	17·8 mol.-% KI 71·9 mol.-% AgBr 10·3 mol.-% AgI
KI–74AgBr,26AgI	eutectic	253°	16·9 mol.-% KI 61·5 mol.-% AgBr 21·6 mol.-% AgI

The triple transition for simultaneous crystallization of (solid solution of AgI–AgBr), (solid solution of KI–KBr), and the compound KI,4AgI is at 317°, and corresponds to the overall composition 20·5 mol.-% KI, 7·1 mol.-% AgBr and 72·4 mol.-% AgI.

In the irreversible reciprocal system potassium iodide–silver chloride[269a] a triple point is observed at 232°, and the composition 43% AgCl, 4% KCl and 53% AgI. A similar point occurs for the components KCl (1%) KI (29·5%) AgI (69·5%) at 240°; in this sub-system a transition point for the compound AgI,4KI occurs at 248°. The binary system AgI–KCl forms a eutectic at 466° with 7·5 mol.-% KCl. The binary pair AgCl–KI shows two eutectics, at 285° (17·9% AgI) and 528° (78·6% AgI), and a compound, AgCl,KI, melting congruently at 625°.

The system potassium iodide–thallous chloride is irreversible in the direction TlCl + KI → KCl + TlI; Fig. 17 illustrates this system. The two triple eutectic points are at 420° (89·5% TlI, 8% KCl, 2·5% KI), and 316° (52% TlCl, 46·5% TlI, 1·5% KCl).[270]

The compounds AgI,6KI and AgI,2KI have been obtained, at −4° and −60°

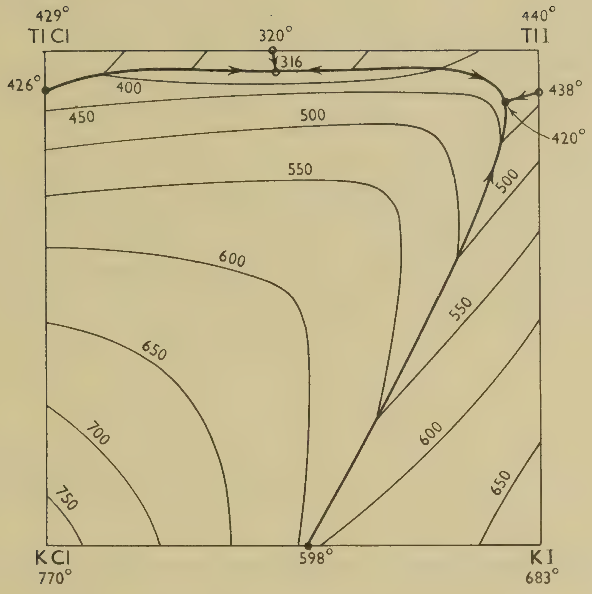


FIG. 17. THE QUATERNARY SYSTEM TlCl–TlI–KCl–KI

respectively, by rapid cooling of ethanol solutions of the components.[271]

The relative solubility of iodine in an organic solvent and in concentrated potassium iodide solution, upon partition, varies with concentration; the results may be expressed by:-

$$\log C_1 = \log \alpha + 1/n.\log C_2.$$

The curves are parallel for different solvents.[272] The distribution ratio, I_{CCl_4}/I_{KI}, at temperatures between 5° and 30°, has been observed to increase with increasing dilution of iodine or potassium iodide.[273]

The properties of the alkali metal polyhalides have been summarized. Their stability is directly proportional to the atomic volume of the metal; thus sodium tri-iodide was thought to be non-existent because the attraction of two iodine atoms in the lattice far outweighs the ability of the sodium to hold three iodine atoms in spatial distribution.[274] It has, however, since been reported, that sodium tri-iodide results from the interaction of sulphamic acid, HSO_3NH_2, and sodium iodide; potassium iodide reacts similarly.[275]

The equilibrium constant for the reaction $I^- + I_2 \rightleftharpoons I_3^-$ has been determined from E.M.F. determinations in iodine concentration cells.[276] The value of $K = I^- \times I_2/I_3^-$ is 0·00140 at 25°, and 0·00072 at 0°: K decreases as the iodine concentration increases, indicating the formation of higher polyiodides. From solubility data it is concluded that the $KI{:}I_2$ ratio increases as the iodide concentration increases.[277] The study of cooling curves for the iodine–potassium iodide system affords no evidence for the existence of a solid polyiodide above 25°.[278] *X*-Ray measurement of the crystals obtained from aqueous iodine–potassium iodide solutions confirms this conclusion.[279] Phase rule studies show that potassium tri-iodide exists as the hydrate, $KI_3{,}H_2O$, at 25°.[280]

In aqueous alcohol, the complex salts KI_3, KI_7 and KI_9 are indicated by viscosity measurements.[281] At 15° in aqueous alcohol the polyiodides KI_4 (hydrated) and K_2I_9 (with 2 (or 3) H_2O) are indicated.[282] A spectroscopic investigation gives the value 3×10^{-5} for the equilibrium constant of KI_3 formation in alcohol at 14°.[283] Computed apparent and partial molal volumes indicate the existence of potassium tri-iodide in methanol solutions.[284]

The solubility study of mixtures of potassium iodide and iodine with organic solvents gave no evidence for the existence of a solid polyiodide between 0·7° and 25°; with benzene as solvent, a ternary addition product, $KI,4I_2,3C_6H_6$ exists.[285]

The Faraday effect for aqueous solutions of iodine in potassium iodide shows a larger specific rotation than the sum of the specific rotations of potassium iodide and iodine, from which it is inferred that KI_3 is present.[286]

From measurements of the spectroscopic absorption limit, the equilibrium constants of the polyhalides, KI_3 and $KClI_2$, have been determined at 5° and 16°C. For the formation of the complexes the constants are as follows:-[287]

KI_3	K (16°)	8×10^2
	K (5°)	7×10^2
$KClI_2$	K (16°)	3·6
	K (5°)	2·3

In 95% ethanol K (14°) for $KI_3 = 2{\cdot}7 \times 10^{-4}$. A later spectrographic method gave the value of K (24°), in aqueous solution, as $5{\cdot}6 \times 10^3$, and it was suggested that the method of ref. 287 was inadequate for quantitative calculation as it dealt only with the absorption limit.[288]

From solubility and density measurements at 25°C. the molar volume of iodine in saturated potassium iodide was found to be 59·96; that of iodine in solid cæsium tri-iodide, CsI_3, has the closely related value of 57·3. The increase of the ratio I_2/KI with increasing concentration of potassium iodide was explained by considering the equilibrium:-

$$I^-(mH_2O) + I_2 \rightleftharpoons I_3^-(m-nH_2O) + nH_2O$$

Thus decreasing the activity of the water should result in an increase in the solubility of iodine. Sucrose effected an increase in the concentration of iodine, up to 2·66N., in saturated potassium iodide.[289]

The polyhalide potassium tetrachloroiodide, $KICl_4$, dissociates in two stages. At 14°C. there is direct decomposition into potassium chloride and iodine trichloride; this is followed by a further dissociation of the trichloride into iodine monochloride and chlorine. The polyhalides $MICl_4$ increase in stability as the radius of the cation M^+ increases; this is in accordance with the thermodynamical calculations of their heats of formation and suggests an error in the lattice energies as calculated by the Kapustinskii formula which places them in the reverse order.[290]

The compounds $KICl_2$, $KIBr_2$ and $KIBrCl$ have been investigated. The equilibrium concentrations of halogen and halogen halide were determined by the method of Abegg and Hamburger[291] and it was deduced that the stability of the anionic complex increased with increasing radius of the alkali metal cation in each case studied.[292]

Ultrasonic studies

The liberation of iodine from aqueous potassium iodide solutions by ultrasonic irradiation varies directly with the duration of irradiation and with increase in the electrical energy.[293] The amount of iodine liberated in a given time is proportional to the ultrasonic field strength;[294] it was considered at first to be inversely proportional to the concentration of the potassium iodide, but this has subsequently been disproved.[295] With stationary waves oxidation occurs at the nodes.[296]

The effect of concentration of potassium iodide upon the amount of iodine liberated in 30 minutes, at a frequency of 600 kc/s and an intensity of 5 watts per sq. cm., has been studied.[297] The amount of iodine increased with concentration, up to 3·5N., and then remained constant. The presence of 0·2% of tryptophan inhibited the oxidation as did also saturating the solution with hydrogen.

The effects of focussing barium titanate transducers and flat quartz transducers on the liberation of iodine from potassium iodide solution and on the depolymerization of poly-styrene in toluene solution have been compared.[298]

When 5% potassium iodide solution acidified with dilute sulphuric acid is exposed for 10 minutes to ultrasonic waves the amount of iodine liberated varies with the frequency, rising to a maximum at 300 kc/s, then diminishing, and remaining constant between 400 and 1000 kc/s.[299,300] Below 20 kc/s, and above 3 Mc/s, oxidation did not occur.[295] Within the frequency range 470 kc/s to 12·87 Mc/s no dispersion of ultrasonic waves was observed in aqueous solutions of sodium chloride, potassium chloride, potassium bromide, potassium iodide and magnesium sulphate, over the temperature range 15° to 55°C. The temperature dependence of wave velocity in these solutions has been studied.[301]

The ultrasonic viscosity η and surface tension λ have been measured at 31°C.; the results are given in Table XC.[302]

TABLE XC - ULTRASONIC VISCOSITY AND SURFACE TENSION OF AQUEOUS SOLUTIONS OF POTASSIUM IODIDE AT 31°C.

Molarity	Density	v	$10^6 b$	$10^3 \eta$	λ
0·1	1·012	1538	42·29	8·23	71·61
0·2	1·022	1528	42·38	8·58	73·02
0·3	1·036	1517	42·45	8·33	74·54
0·4	1·045	1526	41·40	8·10	74·16
0·5	1·059	1523	41·23	8·02	74·85
1·0	1·114	1541	38·25	7·42	75·15

The relationships $\eta = 2 \times 10^2 b$, where b is the adiabatic compressibility, and $\lambda = 1{\cdot}2 \times 10^{-6} \rho . v^{3/2}$ where ρ is the density, and v is the ultrasonic velocity in metres per second, have been established.

Reaction proceeds through radicals released by the decomposition of water[297,303] and organic compounds may compete for these radicals. For example 0·35 mole of ethanol per litre of 0·6N. potassium iodide solution reduced the iodine liberated during a period of irradiation from 8×10^{-5} to 4×10^{-5} mole, and other alcohols, ketones and ethers behaved similarly, showing specific inhibitions.[303] The efficiency of the process has been calculated on the assumption that -OH radicals are first formed with the absorption of 118 kg.-cal./mole.[295] The quantum efficiency in these reactions is very low.[304]

An attempt has been made to relate ultrasonic activity to cavitation within the solution; the dependence on temperature and on frequency support this explanation. Almost ten times as much energy is required to produce a given amount of iodine at 1·4 Mc/s as at 576 kc/s.[305] The heat generated upon ultrasonic irradiation of a potassium iodide solution is always less than that generated in water under the same conditions;[306] the evolution of heat associated with cavitation has been measured.[307]

The importance of dissolved gases in ultrasonic reactions has been discussed,[308] including the effects of air and carbon dioxide.[309]

Acoustic waves of frequency 500 kc/s gave a more rapid liberation of iodine if they were modulated at low frequency (0·2 to 2500 c/s). In this reaction, and also in the depolymerization of polyacrylamide, the rate decreased with increasing modulation frequency.[310]

An ultrasonic interferometer has been used to determine the volume of hydration water of salts;[310a] for potassium iodide, this volume is found to be 58 c.c./mole which agrees well with the previously recorded value of 54 c.c./mole.[310b]

Water is slightly oxidized to hydrogen peroxide by ultrasonic irradiation;[293] nitrous and nitric acids are also formed.[311] Sodium bisulphite and ferrous sulphate solutions are both oxidized by atmospheric oxygen under these conditions.[304,312] Glycine is deaminated, and carbon tetrachloride decomposed.[307,312]

Analysis of the results of many investigations shows many quantitative disagreements which are traced to the effect of experimental details. The effect of differences in the mounting and cutting of the quartz transducers and of frequency variation during irradiation upon the liberation of iodine from potassium iodide solutions has been investigated.[313]

Analysis

Potassium iodide for pharmaceutical use may be evaluated by treating a sample with sodium nitrite and dilute sulphuric acid. After frequent agitation, the mixture is treated with excess sodium bicarbonate solution, and the iodine liberated is titrated with standard arsenious oxide solution.[314] The determination of small amounts of bromide in potassium iodide is difficult; the iodine is best determined by titration with standard potassium iodate in acid solution and in the presence of cyanide ions.[315]

About 0·25g. of the sample is dissolved in 50 c.c. of 5N. sulphuric acid, 1-2g. of sodium chloride is added, and then 10 c.c. of 3·3% potassium cyanide solution. Using 10 cc. of starch solution as indicator, the solution is then titrated with M./40 potassium iodate until colourless. The overall reaction is:-

$$2I^- + IO_3^- + 3HCN + 3H^+ \rightarrow 3ICN + 3H_2O.$$

This is a modification of a method due to Lang.[315a]

Official potassium iodide-iodine solutions may be assayed by titration with standard potassium arsenite solution using starch as indicator; concentrated hydrochloric acid, and a few ml. of chloroform are added and the solution is cooled. Titration with standard iodate is carried out until the chloroform layer is colourless. The potassium iodide content is calculated from the difference between the two titrations.[316]

A modified method for the determination of potassium iodide in iodine-free solutions has been described; it agrees well with established methods and obviates benzene extraction.[317]

The titration of potassium iodide solutions with silver nitrate (by Fajans' method) has been shown to give good results in the presence of nitric acid and sulphuric acid when tropaeolin-OO, sodium alizarinsulphonate, bromophenol blue, formyl violet, or congo red was used as adsorption indicator.[318]

The general requirements for a satisfactory redox primary standard have been considered;[319] potassium iodide has been suggested for this purpose and its reaction with permanganate has been studied. In the presence of cyanide ions, the reaction is stoicheiometric within 0·1%.[320]

The accuracy of potassium iodide-mercuric chloride titrations depends largely upon the concentration; correction factors have been determined.[321]

The presence of iodate in potassium iodide may be detected by shaking 1g. of the salt in 10ml. of water with 3ml. of chloroform and five drops of glacial acetic acid; a pink colour in the chloroform layer indicates the presence of iodate.[322]

Potassium periodate has been used in acid solutions as an oxidizing agent for the volumetric determination of potassium iodide. Carbon tetrachloride is used as indicator; it becomes decolourized at the end-point, owing to the formation of a stable complex ion.[323,324] Sodium metavanadate has also been used in hydrochloric acid solution for the volumetric determination of potassium iodide; iodine monochloride is added as catalyst and preoxidizer, and chloroform is used as indicator.[325]

The reaction between cuprous and cupric ions and potassium iodide has been studied; since it depends upon the reversible equilibrium:-

$$2Cu^{2+} + 2I^{-} \rightleftharpoons 2Cu^{+} + I_2,$$

the potassium iodide concentration must be adjusted according to which copper ion is to be determined. Suitable concentrations are deduced.[326]

The reaction between hypochlorite and potassium iodide may be used for the determination of hypochlorites. If titration is slow it is considered to proceed according to the equation:-[327]

$$3HClO + I^{-} \rightarrow IO_3^{-} + 3H^{+} + 3Cl^{-}.$$

Potassium iodide solutions may be titrated potentiometrically with chloramine-B, the redox electrode being of platinum foil and the reference electrode a saturated calomel half-cell;[328] the same reagent may be used for iodometric titration.[329]

Bromic acid may be titrated potentiometrically with potassium iodide over a wide range of concentrations in sulphuric acid solution but only over a restricted range in hydrochloric acid.[330]

Potassium iodide may be titrated potentiometrically with N/10 silver nitrate using a silver or platinum electrode.[331] Oxidation with alkaline permanganate may also be followed potentiometrically, the iodide being oxidized to periodate.[332] It has subsequently been reported, however, that direct titration is unreliable; addition of excess permanganate and back-titration with a standard thallous salt solution is considered preferable.[333]

Vanadium may be determined by reducing V(V) in phosphoric acid solution to vanadyl(IV) by potassium iodide, and titrating the liberated iodine.[334] A method for the micro-determination of osmium depends upon the fact that osmium catalyzes the reaction between potassium iodide and potassium chlorate.[335] The quantity of osmium may be represented by: $Q = 1{\cdot}22/T + 0{\cdot}092$, at 15°, where T is the time required for transmission at 572mμ to decrease from 60% to 10%. Vanadium(IV) may be determined in a similar way.[336]

With regard to the refractometric analysis of solutions, the increments of refractive index are not constant;[337] in aqueous solution the increment of n per 1% varies for potassium iodide from 0·001299 at 5·31% to 0·001295 at 20·08%.

Uses

The immersion of exposed photographic plates for 2 minutes, before developing, in 4% potassium iodide has been suggested as a method of processing which does not require a dark-room, the unexposed silver halide being thus converted into silver iodide.[338] This device, however, requires very much longer exposures, because of the destructive effect of iodide upon the latent image, and fixation is also very slow.[339] The addition of 2 to 12 mg./l. of colour-film developing solution increases the density in the yellow layer.[340]

A scintillation counter sensitive to neutrons and to γ-rays consists of powdered potassium iodide activated with thallium.[341]

Venezuelan marine salts contain 95% to 99% of sodium chloride, together with magnesium and calcium salts. Addition of potassium iodide to these salts, in order to produce iodized salt, was not satisfactory, because of the poor stability of the potassium iodide.[342]

A mixture of 1 part of potassium iodide and 1·3 parts of mercury iodide dissolved in 0·25 part water gives a liquid of density 3·3, suitable for the identification of minerals by flotation.[343]

The effect of 1% by weight of potassium iodide on the grain growth of alumina has been studied at temperatures of firing between 1300° and 1700° and the results tabulated.[344] Potassium iodide (0·01 to 0·1%) improves the fining of optical high-density glass, and prevents wetting of the crucible by the batch of glass being treated.[345]

Soaking or spraying fruit with dilute aqueous potassium iodide, and subsequent treatment during storage with an oxidizing non-corrosive gas such as ozone, prevents deterioration; for long periods of storage, the iodide may be replenished periodically.[346]

The system potassium iodide-uranyl sulphate-water constitutes a chemical actinometer; photolysis proceeds according to the reaction:-

$$UO_2SO_4 + 2KI + H_2O + O \rightarrow K_2SO_4 + UO_2(OH)_2 + I_2$$

A trace of sodium chloride accelerates the reaction.[347]

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SECTION LIV

POTASSIUM SULPHIDES

By A. R. BURKIN

Preparation

Laboratory methods of preparing the various sulphides have centred around the use of solvents other than water and the establishment of the fact that the various products are true chemical compounds.

A phase rule study (Mellor, II, 630) of the system K_2S–S shows the existence of a range of sulphides of formula K_2S_n. Those with $n = 2$, 3 or 4 decompose slightly at their melting points; K_2S_6 is largely decomposed at its m.p. while K_2S (m.p. 840°C.) and K_2S_5 (m.p. 206°C.) are stable at these temperatures.[1] The m.p. of K_2S has independently been given as 912°C. (see below and ref. (2).)

By permitting potassium metal to react with an excess of sulphur under boiling toluene, filtering, washing and drying, all in an atmosphere of purified dried hydrogen, K_2S_5 is produced.[3] Under similar conditions sodium gives Na_2S_3. The same method has been reported as giving mixtures corresponding to $K_2S_{4.7}$.[4]

In water or aqueous alcohol (Mellor, II, 638) crystallisation of solutions prepared by dissolving the required amount of sulphur in the K_2S solution followed by evaporation at room temperature in vacuo over phosphorus pentoxide gives crystals of the following compounds:[1] $K_2S_2, 3H_2O$ (cream coloured, acicular); K_2S_3 (orange-red prisms); $K_2S_4, 3H_2O$ (golden yellow, glistening tabular); $K_2S_4, 2H_2O$ (lighter than the preceding) and K_2S_5, H_2O (orange-red minutely crystalline). The relationship between the sulphur:potassium ratio and the product crystallising from gently boiling solutions of sulphur and K_2S in absolute alcohol is as follows:

S:K	<1·63	1·63 – 2·0	2·0 – 2·5	>3·0
Product	K_2S_3	$K_2S_3 + K_2S_5$	K_2S_5	K_2S_5 + S

Orange-red, highly hygroscopic crystals of K_2S_5 have been produced[5] by dissolving 1 g. of potassium metal in alcohol, saturating the solution with dry hydrogen sulphide, adding 1·64 g. of sulphur and boiling the reaction mixture for an hour in a current of hydrogen. The action of sulphur on alcoholic solutions of KHS gives[1] only K_2S_5 when the ratio S:KHS is 2:1 while with less sulphur mixtures of KHS and K_2S_5 are obtained. In one investigation[4] the *X*-ray diffraction patterns of a number of sulphides were obtained and it was shown that these are all definite compounds and that only one modification of K_2S_2 was obtained. The compounds and methods of preparation were as follows. K_2S_3 and K_2S_5 were prepared by adding the calculated amount of sulphur to a solution of K_2S in absolute alcohol and precipitating the insoluble product. K_2S_6 was obtained by melting K_2S_5 and sulphur in vacuo while the reaction between sulphur and potassium in liquid ammonia was used for K_2S_2 and K_2S_4. The action of potassium on molten sulphur gives no compound higher than K_2S_4[1], while sulphur and anhydrous potassium carbonate was reported as giving "polysulphide" and thiosulphate at 250°C. and, at 600°C., "polysulphide" and sulphate. The reaction between sulphur and potassium hydroxide gave similar results.

Gradual addition of sulphur to potassium amide dissolved in liquid ammonia at −33° gives a yellow precipitate which dissolves on adding more sulphur.[6] The course of the reaction is said to be:

$$6KNH_2 + 3S \rightarrow 2K_2S(\text{ppt.}) + S(NK)_2,NH_3 + 3NH_3$$

followed, if the reaction is carried out rapidly, by

$$6KNH_2 + 12S \rightarrow 2K_2S_4 + S_4(NK)_2 + 4NH_3$$

The latter step gives K_2S_3, if the reaction takes place slowly. It had previously been reported[7] that the reaction between sulphur and a solution of potassium in liquid ammonia gave K_2S, K_2S_2, K_2S_4 and higher sulphides of uncertain composition. Potentiometric titration of solutions of potassium sulphide in ammonia with solutions of the alkali metals in ammonia shows that K_2S, K_2S_2 and K_2S_4 are formed.[8] Analysis of K_2S produced by the reaction between potassium and sulphur in liquid ammonia both in the absence and presence of hydrogen showed it to contain K_2S, 95·5; $K_2S_2O_3$, 2·5; K_2SO_3, 1·5; S, 0·2%, with traces of K_2SO_4 and KNH_2.[2] Aqueous solutions of K_2S always contain sulphites and thiosulphates owing to oxidation by dissolved air.[9,10] When attempts are made to produce sulphides of metals in high oxidation states, oxyacids of sulphur may also be produced. Thus the reaction between PbO_2 and aqueous K_2S solution at ordinary temperatures proceeds slowly, the product being probably PbS.[11] An analytical procedure for alkali sulphides using oxidation to sulphate has been described.[12] The sample is dissolved in boiled-out water and a known amount of 0·1 N-sodium hydroxide and some hydrogen peroxide is added to an aliquot. After boiling to remove excess peroxide the unused alkali is determined. The reaction used is written

$$S_x{}^{--} + (2x - 2)OH^- + (3x + 1)H_2O_2 \rightarrow xSO_4{}^{--} + 4xH_2O$$

and 1 ml of 0·1 N-alkali is equivalent to 1·603 mg. of polysulphide sulphur.

A few developments in industrial methods of preparation have been reported. The waste gases from carbon disulphide production contain hydrogen sulphide which is absorbed in hot concentrated alkali metal hydroxide solution. Free alkali is added to the final liquor to form potassium disulphide which deposits on cooling the solution.[13] The disulphide is also produced when finely powdered rocks containing potassium and aluminium as silicate are reduced with metallic aluminium and sulphur.[14] Reduction of the mineral langbeinite ($2MgSO_4,K_2SO_4$) with excess carbon at about 700–800°C. produces K_2S, or with sulphur produces a mixture of sulphides and sulphur dioxide.[15] Polyhalite ($K_2SO_4,MgSO_4,2CaSO_4,2H_2O$) reduced by natural gas and extracted with water gives solutions containing K_2S and KHS.[16]

Physical Properties

The degree of hydrolysis of aqueous K_2S solutions has been determined by measuring the velocity of hydrolysis of ethyl acetate.[17] The hydrolytic constant at 0° is 15, a 0·833 N. solution of K_2S being 95% hydrolysed. From the results the second dissociation constant of hydrogen sulphide has been calculated as 6×10^{-17}

The decomposition of hydrogen peroxide is strongly catalysed by colloidal solutions of $Cu_2Fe(CN)_6$ and solutions of the alkali sulphides increase further the catalytic activity.[18]

Carbon dioxide and hydrogen sulphide are often removed from industrial gases by absorption in dilute aqueous solutions of potassium or sodium carbonate. For potassium salts the following equilibrium constants are involved:

$$K_1 = (KHCO_3)^2/(K_2CO_3)P_{CO_2},$$
$$K_2 = (KHCO_3)\,(KHS)/(K_2CO_3)P_{H_2S},$$
$$K_3 = (KHCO_3)P_{H_2S}/(KHS)P_{CO_2}.$$

Values of all three constants have been determined[19] over the concentration range 0·2 to 2 N. and from 0 to 60°C., the calculated heats of reaction agreeing well with the published heats of formation. The value of K_1 is nearly independent of cation concentration.

Temp. °C.	0·0	10·0	20	30	40	50	60·4
K_1	0·70	0·44	0·282	0·182	0·132	0·093	0·072

The value of K_2 is independent of the concentration of KHS over the concentration range 0·05 to 0·4 gram moles per litre and the values corrected to a potassium ion concentration of 2N. are

Temp. °C.	0·5	9·9	20·7	29·5	39·5	49·6	59·6
K_2	0·147	0·120	0·098	0·086	0·073	0·0635	0·057

Extrapolation to zero concentration gives K_2 at 25°C. = 0·15. Independent measurements[20] give at 25°C. K_2 = 0·074 mol/l.mm. The relationship between the vapour pressure of hydrogen sulphide P and the concentration of hydrogen sulphide in 2 N-potassium carbonate, c, at equilibrium between 25° and 60°C. is given by the equation $P = 0{\cdot}714(t + 43)\,c^{2\cdot88}$. The relation between K_2 and temperature is expressed as $\log K_2 = (2800/4{\cdot}576\,T) - 3{\cdot}2$.

The stereochemistry of the potassium sulphides is said[21] to be best explained on the basis that two types of sulphur atoms are involved, the end members of the polysulphide chain, with a partial molar volume of about 20 c.c. and those within the chain with partial molar volume about 12 c.c.

K_2S has the cubic calcium fluoride structure with a = 7·35 A.[22] or 7·391 A.[23] It is not dimorphous in the range 25° to 200°C.

KSH exists in two forms[22] with a transition temperature of about 170°C. The low temperature form has a rhombohedral unit cell with a = 4·37 A. and α = 68°51′. The high temperature, cubic form has the sodium chloride structure with a = 6·60 A. The SH group in this modification has spherical symmetry with radius 1·99 A.

An investigation of the system K_2S–K_2SO_4[2] shows two eutectics, one at 587°C. with 56% K_2S and the other at 730°C. with 72·5% K_2S. A compound $K_2SO_4, 3K_2S$ exists, with melting point between 755° and 759°C. Mixed crystals are formed with up to 30% K_2S. The freezing point of K_2S is given as 912°C., which is believed to be not more than 10° too low.

The densities of a number of potassium sulphides are as follows,[4] mean values being given: K_2S_6, d_{20} = 2·02; K_2S_5, d_{20} = 2·128; K_2S_4, after heating at about 130°C., d_{20} = 1·93, after melting, d_{20} = 2·04; K_2S_3, d_{20} = 2·102; K_2S_2, after heating in vacuo at about 140°C., d_{20} = 1·79, after melting, d_{20} = 1·973.

The magnetic properties of the potassium sulphides have been studied at room temperature and at −183°C.[24] At low temperatures K_2S_3 behaves in "an unusual manner" and appears to be ferromagnetic below −50°C. A series of solid solutions comprising the substance described as $K_2FeCu_3S_4$, having a tetragonal lattice with c/a 1·182, is paramagnetic, containing ferric iron, whereas the thio-salts of copper, KCuS, KCu_4S_3 and $KCuS_4$ are diamagnetic.[25]

The dielectric constant of K_2S is 6·85 after drying for three days over phosphorus pentoxide.[26]

Rotation of the plane of polarisation produced when plane polarised light of wave-length 546 mμ is passed through a solution of K_2S in a magnetic field (Faraday effect) has been investigated[27] as has the photoconductivity of the solid sulphide.[28] Alkali polysulphides produced by thermal reduction of the sulphates fluoresce in the red when irradiated by light of wave-length 366 mμ or in the blue with 254 mμ (mercury lines).[29] At all temperatures the luminescence intensity is proportional to the intensity of the exciting radiation so that the mechanism of the luminescence is unimolecular. The causes and mechanisms of the luminescence processes are, however, different.

Applications

Alkali metal sulphides are used for treating surfaces for a number of applications. Copper alloys have been treated with K_2S solutions at 40–50°C. followed by neutralisation in sulphuric acid and washing to give a uniform deposit of copper sulphide. This is then treated with cold ammonium chloride solution to produce the desired greenish-white surface coating.[30] Oxide and nitride coatings can be removed from titanium metal surfaces by immersing the metal in a bath of molten sodium or potassium polysulphide at 250–500°C. for about ten minutes. The treatment can be prolonged to an hour if the sulphide bath is "buffered" with, for example, magnesium halide.[31] Similarly silver can be removed from mirrors by immersion in hot alkali sulphide solutions containing alkali or solvent to soften the protecting coating.[32]

Rubber-like solids can be produced from alkali sulphides by condensation with saturated alkyl halides containing an epoxy group.[33] Condensation with dichloroethyl acetal has also been used.[34] Oils of animal, vegetable or mineral origin can be sulphurised by treatment with an alkali metal sulphide at 60–180°C. followed by sudden cooling.[35]

Alkali metal sulphides are oxidised by halopicrins giving sulphur, carbon disulphide and carbonyl sulphide as well as compounds not containing sulphur. A set of equations has been proposed[36] to cover the reactions occurring as well as those involved in the more complex case of the reaction between KHS and chloropicrin.

Reaction of alcoholic K_2S with tetrabromotetramethylmethane gives 2–thio–2,6,7–trithia–4–spirooctane[37] while anhydrous K_2S_5 with allyl iodide gives diallyl pentasulphide.[38] A number of aromatic halogen compounds behave similarly. Lactones or lactone-like compounds containing aromatic groups when heated in the anhydrous liquid state with sufficient KHS to react directly with half of the lactone give dicarboxylates which may be converted to the free dicarboxylic acid.[39] Thus, γ-butyrolactone gives thiodibutyric acid. Tetrahydrothiophenes can be prepared from 1, 4 difunctional compounds, for example $Br(CH_2)_4Br$, by reaction with K_2S.[40] Production of pure, anhydrous polysulphides of the alkali metals has enabled alkyl polysulphides to be prepared by reaction with the alkyl halide.[41]

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SECTION LV

POTASSIUM SULPHATE

By W.P. DOYLE

Preparation

The history of the manufacture of potassium sulphate up to 1922 has been described.[1]

The manufacture of potassium sulphate has been the subject of some 120 patents and papers. In the following summary of the extensive literature references only are given.

More processes for the extraction of potassium sulphate from kainite[2,3] and from kieserite[4-8] (Mellor, II, 659) have been patented. A number of patents relate to the production of potassium sulphate from other Stassfurt-type potash salts such as langbeinite,[9-16] $2MgSO_4,K_2SO_4$, polyhalite,[17-30] $MgSO_4,K_2SO_4,2CaSO_4,2H_2O$, and syngenite,[31,32] $K_2SO_4,CaSO_4,H_2O$.

Other publications describe processes for the conversion of potassium chloride to potassium sulphate. Reagents suggested for this purpose include sulphuric acid,[33-37] sulphur dioxide,[38,39] potassium bisulphate,[40] ammonium sulphate,[41-44] magnesium sulphate,[45-52] calcium sulphate,[53-56] sodium sulphate,[57-62] and glaserite.[63-65]

A few processes for the production of potassium sulphate from saline lake brines[66-69] and from sea water[70] have been patented.

The extraction of potassium sulphate from alunite,[71-90] $K_2SO_4,Al_2(SO_4)_3,2Al_2O_3,6H_2O$, has been described. In most of the processes suggested aluminium sulphate is converted to the oxide by calcining the ore or by treating it with ammonium hydroxide, the aluminium oxide is removed by filtration and potassium sulphate obtained from the filtrate.

The production of potassium sulphate from silicates,[91-97] jarosite,[98,99] potash alum,[100-103] gypsum[104] and dolomite,[104] calcium sulphate[105] and potassium hydroxide, cane molasses,[106,107] and sunflower stems[108] has been described.

The possibility of separating potassium sulphate from sodium chloride by flotation methods[109-112] has been investigated.

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Physical Properties

The crystal structure of potassium sulphate has been determined;[1-7] it has a simple orthohombic lattice with four molecules per unit cell. The axial lengths have been determined as:-[2]

$$a = 5{\cdot}28\text{A};\quad b = 10{\cdot}25\text{A};\quad c = 7{\cdot}50\text{A};$$

and as:-[6]

$$a = 5{\cdot}85\text{A};\quad b = 10{\cdot}06\text{A};\quad c = 8{\cdot}33\text{A}$$

The space group has been variously reported as[3] $2Di - 13$, as[2] probably B_h^{13} as V_h^{13}, and as[4] V_h^{16}, the last result having been confirmed.[7] The positions of the atoms in the lattice have been determined.[4,5] The characteristic twinning of potassium sulphate crystals has been explained in terms of its structure[4] and the frequencies of occurrence of various faces of potassium sulphate crystals have been correlated with its crystal structure.[8] Mixed crystals of potassium sulphate and rhombic ammonium sulphate have been investigated by the *X*-ray crystal powder method.[19]

The temperature at which potassium sulphate is transformed from orthorhombic to hexagonal has been reported as:-[10]

586 ± 2°C., as[11] 583 ± 1°C., and as[12] about 600°C.

The heat of transformation, calculated from the experimental value of the high temperature heat content, is[18] 1,940 g.-cal. The nucleation frequency for the polymorphic transition has been qualitatively investigated.[14] Other transformations occur[10] at about 300°, 350° and 449°C.

Under conditions where small opaque crystals are normally formed, potassium sulphate can be caused to grow from solution as larger transparent crystals by the addition of 0·001 - 0·5 mole % of various foreign cations;[15,16] the order of decreasing effectiveness is:-[16]

UO_2^{2+}, VO^{3+}, Cd^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Cu^{2+}, Mg^{2+}, Bi^{3+}

For Cd^{2+} and Mn^{2+}, the amount of foreign cation included in the potassium sulphate crystals increases linearly with the concentration of the cation in the solution.[16] Certain cations, Fe^{3+}, Cr^{3+} and Ti^{3+}, hinder the crystallization of potassium sulphate.[15] The influence of the RO_4 ion and related ions on the habit of potassium sulphate crystals has been investigated;[17] the $S_2O_3^{2-}$ ion has a very marked effect on the (001) planes and in concentrated solutions causes the deposition of thin wafer-like crystals; the $S_2O_6^{2-}$ ion also has a strong effect on the (001) planes while NO_3^- and ClO_3^- ions affect both the (001) and the (010) planes; the $Cr_2O_7^{2-}$ ion enlarges (010) and causes distortion of (021) planes; the following ions have no effect:- PO_4^{3-}, AsO_4^{3-}, ClO_4^-, MnO_4^-, CO_3^{2-}, BrO_3^-, $B_4O_7^{2-}$, $H_2PO_4^-$, $H_2AsO_4^-$, HPO_4^{2-} and $HAsO_4^{2-}$. Dyes which are effective in modifying the crystal habit of potassium sulphate have been listed;[18,19] the effective functional groups, the mechanism of habit change and the effect of molecular configuration have been discussed.[18] The effect of agar-agar and of gelatin on the crystallization of potassium sulphate has been investigated.[20,21] The effect of supersaturation on the habit of potassium sulphate crystals has been investigated.[22] Safranine-resorcinol and phenol in a potassium sulphate solution form tufts of needle-like crystals which are included in the crystallizing potassium sulphate.[23]

When a glass rod was dipped into potassium sulphate solution, crystals climbed on the rod by evaporation;[24] the height, weight and density of the crystalline crust were compared with those of other salts and the results are tentatively explained in terms of the influence of the ions and the undissociated part of the salts on the surface tension. Cyclic twin formations have been described using potassium sulphate as an example;[25] for potassium sulphate the twin planes are (110) and $(1\bar{1}0)$; serial twins were not observed. Potassium sulphate and potassium beryllium fluoride, K_2BeF_4, form mixed crystals in all proportions; this is to be expected because the sulphate ion and the complex beryllium fluoride ion, BeF_4^{2-}, are isoelectric isoteres.[26] Similarly the sulphate ion and the monofluorophosphate ion, PO_3F^{2-}, are isoelectric isoteres, and potassium sulphate and potassium monofluorophosphate form mixed crystals in all proportions.[27]

The refractive index, n_D^{20}, of crystalline potassium sulphate is[28] 1·4950 and the molar refraction is 19·07. Potassium sulphate has been used to test a very accurate interferometric method for the determination of refraction in crystals.[29] Pure potassium sulphate does not show crystalloluminescence;[30] neither does pure sodium sulphate, but the formation of crystals of the composition $2K_2SO_4,Na_2SO_4$ is accompanied by luminescence. Solid potassium sulphate which has been exposed to ultra-violet radiation can affect a photographic plate.[31] Potassium sulphate is only slightly coloured by irradiation if not submitted to pressure, but it becomes purple if first compressed and then irradiated; if melted, allowed to solidify and then irradiated it becomes green.[32] The scattering of light by solutions of potassium sulphate of concentration greater than 0·1 molar has been measured;[33] the experimental value of the Rayleigh constant is less than the theoretical value obtained from a modified Debye formula. The Raman spectra of crystalline potassium sulphate and of its aqueous solution have been measured and compared;[34] the frequency shift in the solid is 992·1 cm.$^{-1}$ and is less than that in 1 – 2N aqueous solutions.[35] From a study of the ultra-violet absorption spectrum of potassium sulphate vapour, it has been concluded that in the vapour state the bonding is largely covalent.[36]

A suspension of potassium sulphate in benzene or toluene has a positive electric birefringence.[37] The parallel and transverse components of magnetization have been measured for varying orientation of the magnetizing field in chosen planes of potassium sulphate crystals.[38] During the reaction of potassium sulphate with sulphuric acid to form potassium bisulphate, the molecular diamagnetism decreases[39] by $4{\cdot}47 \times 10^{-6}$.

A surface examination of potassium sulphate with exo- and photo-electrons has been described.[40] Crystals of potassium sulphate having freshly broken surfaces when dissolved in water cause a markedly greater alkaline reaction towards phenolphthalein than crystals with aged surfaces.[41]

The densities of crystalline potassium sulphate at various temperatures are given in Table I; by extrapolation, the density at absolute zero is[42] 2·72.

TABLE I. DENSITY OF SOLID POTASSIUM SULPHATE

t°C.	Density	Reference
21	2·660	42
20	2·665	28
20	2·6617	43
–78	2·693	42
–195	2·716	42

The mean coefficient of thermal expansion of solid potassium sulphate is[44] 13×10^{-5} from 21° to –78°C., 7×10^{-5} from –78° to –195°C. and, by extrapolation, 3×10^{-5} from –195° to –273°C. The strength of potassium sulphate crystals has been measured.[44] The compressibility of solid potassium sulphate has been measured up to 12 kilobars; the results can be represented by the equation:-

$$10^5K = 331{\cdot}8p - 3{\cdot}83p^2$$

where p is the pressure and K is the relative volume change.[45] The vapour pressure of molten potassium sulphate is[46] 0·4mm. of mercury at 1130°C.

The melting point of potassium sulphate has been reported as[12] 1080°C., and as[11] 1069·1°±0·5° C.; the latter value has been confirmed.[47] The heat of fusion, calculated from experimental values of the high-temperature heat content, is[13] 8,760g.-cal. The specific heat of solid potassium sulphate has been measured[48] from 51° to 298° abs.; values, in calories per gram formula mass, are given in Table II.

TABLE II. SPECIFIC HEAT OF SOLID POTASSIUM SULPHATE

T (° abs.)	Specific Heat
52·7	10·73
80·2	16·29
104·7	19·34
124·2	21·15
154·7	23·51
175·0	24·83
205·3	26·61
225·5	27·74
255·1	29·23
276·0	30·26
295·4	30·99

The specific heat relations for solid potassium sulphate are:-[13]

$$K_2SO_4\ (\alpha) : C_p = 27{\cdot}4 + 0{\cdot}2552T - 352{,}000/T^2$$

$$K_2SO_4\ (\beta) : C_p = 26{\cdot}80 + 0{\cdot}02010\,T$$

and for liquid potassium sulphate:-

$$K_2SO_4\ (l) : C_p = 47{\cdot}28$$

The free energy of formation, ΔF_{298}, of potassium sulphate as determined from e.m.f. and vapour pressure measurements is[49] −313,532g.-cal. and as determined from specific heat measurements is[48] −314,600g.-cal. Free energy increments above 298·16°abs. computed from experimentally determined heat contents[13] are given in Table III.

TABLE III. HIGH-TEMPERATURE HEAT CONTENTS, ENTROPY AND FREE ENERGY INCREMENTS OF POTASSIUM SULPHATE

T° abs.	$H_T - H_{298\cdot16}$ g.-cal./mole	$S_T - S_{298\cdot16}$ g.-cal./deg./mole	$F_T - F_{298\cdot16}$ g.-cal./mole
400	3,400	9·79	−4,790
700	15,390	32·05	−23,920
1000	31,630	51·32	−49,170
1300	46,390	64·18	−79,120
1600	69,840	80·89	−114,260
1700	74,330	83·62	−126,700

The heat of formation, ΔH_{298}, of potassium sulphate is[49] −339,670g.-cal. The entropy of potassium sulphate at 298·16°abs. has been evaluated as[49] 51·5 from e.m.f. and vapour pressure measurements and as[48] 42·0±0·6 from specific heat measurements. Entropy increments above 298·16°abs. computed from experimentally determined heat contents[13] are given in Table III. The heat contents of potassium sulphate have been determined[13] from about 473° to 1700°abs. and are also given in Table III. Other thermodynamic studies on potassium sulphate have been reported[50] and the thermodynamic properties of potassium sulphate have been critically discussed.[51]

The heat of reaction for the formation of the double salt K_2SO_4,Li_2SO_4 has been discussed thermodynamically.[52] The heat of formation of anhydrous potassium alum, $KAl(SO_4)_2$, from the elements is[53] −589,170g.-cal. per mole and that of potassium alum, $KAl(SO_4)_2,12H_2O$, is[53] −1,447,700g.-cal. per mole; the heat of formation of potassium alum from the elements and liquid water is[53] −627,900g.-cal. per mole. The following heat of reaction values have been derived.[53]

$$0{\cdot}5\,K_2SO_4 + 0{\cdot}5[Al_2(SO_4)_3,6H_2O] + 9H_2O\ (l) \rightarrow KAl(SO_4)_2,12H_2O;$$

$$\Delta H = -27{,}430 \pm 50\text{g.-cal.}$$

$$0{\cdot}5\,K_2SO_4 + 0{\cdot}5\,Al_2(SO_4)_3 + 12H_2O \rightarrow KAl(SO_4)_2,12H_2O;$$

$$\Delta H = -46{,}060 \pm 130\text{g.-cal.}$$

$$0{\cdot}5\,K_2SO_4 + 0{\cdot}5\,Al_2(SO_4)_3 \rightarrow 2KAl(SO_4)_2;$$

$$\Delta H = -7{,}340 \pm 230\text{g.-cal.}$$

$$KAl(SO_4)_2 + 12H_2O\ (l) \rightarrow KAl(SO_4)_2,12H_2O;$$

$$\Delta H = -38{,}720 \pm 210\text{g.-cal.}$$

The heat of solution of potassium sulphate ($K_2SO_4 \rightarrow K_2SO_4,400H_2O$) at 20°C. is[54] −6,284 ± 4g.-cal.; the value of the heat of solution depends on the thermal history of the salt[54] and this phenomenon is explained on the basis of the formation of metastable mixtures of the polymorphic forms. The integral heat of solution of potassium sulphate in water at 25°C. has been measured over the concentration range 0·0693 to 0·6667 molar and the results of previous measurements have been critically analysed.[55] For potassium sulphate, the heat produced by the dissolution of the last mole to make a large amount of saturated solution is[56] −6,750g.-cal. at 0°C. and −5,900g.-cal. at 18°C.; the heat of solution of potassium sulphate in a large quantity of water is[56] 8,020g.-cal. at 0°C. and 6,400g.-cal. at 18°C. Le Chatelier's theorem, that $(ds/dt)/(ds'/dt) = Ls/L's'$ where s and s' are the solubilities of the two components of the solution and L and L' the respective molar heats of solution at the eutectic point, has been verified experimentally by comparing the experimentally determined value of L for potassium sulphate, −6,600g.-cal. with that calculated from the experimental values of the other terms of the equation.[57] The theoretical heat of solution of potassium sulphate, derived from thermodynamic constants, is[49] −3,209g.-cal. The integral heats of dilution of potassium sulphate at 25°C. in the concentration range[58] 0·1 to 0·0001 molar are given in Table IV.

TABLE IV. INTEGRAL HEAT OF DILUTION OF POTASSIUM SULPHATE AT 25°C.

Initial Concentration (molarity)	Final Concentration (molarity)	Ht. of Dilution (g.-cal./mole K_2SO_4)
0·00625	0·0001645	117
–	0·0003250	105
0·0125	0·0003290	144
–	0·0006494	129
0·025	0·0006580	165
–	0·001299	145
0·05	0·001316	170
–	0·002597	143
0·1	0·002632	146
–	0·005195	112

The heats of dilution of potassium sulphate in the concentration range[59]

0·5 to 0·01 molar are given in Table V.

TABLE V. HEAT OF DILUTION OF POTASSIUM SULPHATE

t°C	Initial Molar Concentration	Ht. of Dilution	(g.-cal./mole K_2SO_4)
		Dilution of 50x	Dilution of 25x
0 (approx.)	0·25	−679	−660
	0·025	−12	−20
10 (approx.)	0·25	−371	−389
	0·025	81	73
20 (approx.)	0·5	−373	−408
	0·25	−80	−115
	0·1	96	69
	0·05	137	112
	0·025	150	130
	0·0125	131	124

The first, intermediate, and last integral heats of dilution have been determined[60] at 0°C. and at room temperature. The heat capacity of aqueous potassium sulphate solutions has been measured in the concentration range 0·0385 to 0·6500 molar at 25°C. and for the concentration, $K_2SO_4,400H_2O$, at 20°C. and the results of previous measurements have been critically reviewed.[55]

The integral heat of solution of 25°C. of 1 gram-equivalent of potassium sulphate in a mixture of 50 moles of water and m moles of hydrogen chloride is[61] −3,010, −5,230, −5,340, −5,190, −5,060 and −4,880g.-cal. at m = 0, 0·32, 0·83, 1·68, 2·38 and 3·46 respectively; the results are discussed in relation to ionic hydration. The heat of solution of potassium sulphate in a solution containing 1 mole of hydrogen chloride in 12·68 moles of water is[53] 9,534 ± 18 g.-cal. per mole and that in a solution containing 1 mole of potassium hydroxide in 277·3 moles of water is[53] 5,948 ± 27g.-cal. per mole. The heat of solution at 25°C. of 5 moles of potassium sulphate in a solution containing 5 moles of magnesium sulphate in 1000 moles of water is −5,780g.-cal. and that in a solution of 45 moles of magnesium sulphate in 1000 moles of water is −4,380g.-cal.;[62] the heat of solution of magnesium sulphate heptahydrate, $MgSO_4,7H_2O$, in saturated aqueous potassium sulphate solution has been determined.[62]

From measurements of heat of solution and the value of the lattice energy, the total heat of hydration of potassium sulphate has been critically selected as 401kg.-cal. per mole; this value has been used to obtain the heat of hydration of the simple potassium ion, K^+, 80kg.-cal. per g. ion and the results have been discussed in relation to the nature of the hydration sphere.[63]

The solubility of potassium sulphate in water is[64] 9·21% at 15°C., 9·91% at 20°C., 10·69% at 25°C. and[65] 12·54% at 30°C. The solubility of potassium sulphate in water at temperatures above 100°C. has been determined;[66] the solubility (weight percentage) which is 25·4 at 179°C., rises to 26·4 at 289°C. falls slightly to 23·3 at 310°C. and then falls steeply to 3·9 at 357°C. The velocity of solution of potassium sulphate in water has been measured[67, 68] and a constant of the velocity of solution in the equation of solution of a spheroidal body has been calculated.[69] The experimental value of the supersaturation of potassium sulphate at 20°C. is 0·37 and the theoretical value is 0·21; these results have been discussed in relation to the stability of supersaturated salt solutions.[70] The maximum concentrations of supersaturated solutions of potassium sulphate and of other salts obey Le Chatelier's solubility law and are considered as what is termed the second solubility of the substance.[71] The velocity of crystallization from supersaturated solutions of potassium sulphate has been determined.[72] Quinoline yellow causes supersaturation of potassium sulphate solution.[73] On the basis of a mathematical treatment of supersaturation, solubility values for potassium sulphate have been calculated for stable and metastable equilibrium at various temperatures.[74] The effect of pressure up to 10 kilobars on the solubility of potassium sulphate in water can be calculated theoretically from measurements made at 1 kilobar.[75] From compression measurements on aqueous potassium sulphate solutions at 25°C., the solubility, calculated by the thermodynamic method, increases to a maximum of 16·3% potassium sulphate by weight at 3800 bars.[76] The room temperature solubility of potassium sulphate in water at pressures up to 10,000 atmospheres has been calculated thermodynamically and satisfactory agreement with experiment obtained.[77]

The solubility of potassium sulphate in 1N-hydrochloric acid is[78] 16·08% by weight at 20°C. Potassium sulphate is precipitated from 0·5N-hydrochloric acid solution by making the solution 80% with respect to ethyl alcohol if the molarity of the solution with respect to potassium sulphate is greater than 0·04 and from 1·0N-hydrochloric acid if the molarity of the solution is greater than 0·09.[79] The solubility of potassium sulphate in aqueous ammoniacal solution decreases as the ammonia content increases;[80] at 20°C. the solubility which is about 11 g. of salt in 100 g. of water containing no ammonia, decreases to practically zero in a solution of 30 g. of ammonia in 100 g. of water. The solubility of potassium sulphate in a solution saturated with respect to sodium sulphate is[81] 11·1 g. per 100c.c. at 18°C. The solubilities of potassium sulphate in water–hydrogen peroxide mixtures[82] at 25°C., in water–methyl alcohol mixtures[82] at 25°C., and in water–ethylene glycol mixtures[65] at 30°C. are given in Table VI.

TABLE VI. SOLUBILITY (*S*) OF POTASSIUM SULPHATE IN SOME MIXED SOLVENTS

Hydrogen Peroxide-Water (25°C.)		Methyl Alcohol-Water (25°C.)		Ethylene Glycol-Water (30°C.)	
mole fraction of H_2O_2	*S* (molality per 1000g.)	mole fraction of CH_3OH	*S* (molality per 1000g.)	% Glycol	*S* (g.-per 100g. solvent)
0·0000	0·6905	0·0000	0·6905	0·00	12·54
0·0899	1·287	0·0572	0·3049	4·67	10·91
0·1955	1·945	0·0909	0·1933	9·81	8·83
-	-	0·1321	0·1134	19·76	6·00
-	-	0·1941	0·0536	30·01	3·81
-	-	0·2735	0·0221	39·53	2·47
-	-	0·4570	0·00342	50·48	1·47
-	-	-	-	66·03	0·63
-	-	-	-	100·0	0·00

Potassium sulphate is readily soluble in anhydrous hydrogen fluoride[83] at 14 to 18°C, The solubility of potassium sulphate in liquid ammonia at 25°C. is[84] zero. The solubility of potassium sulphate in methyl alcohol, ethyl alcohol, acetone, acetic ester, ethyl ether[85] and in ethylene glycol[85] (Table VI) has been measured.

The solubilities of the following substances in aqueous potassium sulphate solutions have been determined:- sodium sulphate,[81] potassium permanganate,[86] cupric iodate,[87] silver bromate,[88] calcium iodate,[89] calcium oxalate,[90] zinc sulphate,[81] thallium picrate,[91] cerous iodate,[92] lead sulphate,[93] and iodine.[94] The solubility of di-sodium hydrogen arsenate in aqueous systems containing potassium sulphate has been investigated.[95] Potassium sulphate raises the solution temperature of the phenol–water system.[96] The anomalous results found in solubility experiments on cobaltammines in potassium sulphate solution have been interpreted by considering the influence of higher terms of the Debye-Hückel theory in the case of unsymmetric valence type electrolytes.[97]

Several phase equilibria studies of systems containing potassium sulphate have been made. Binary systems were studied and the results obtained are as follows:-

K_2SO_4 - H_2O. The system has been investigated[76] under pressure at 25°C.; the solubility curve intersects the freezing pressure curve of ice$_{VI}$ at 10,750 bars and 13·3% of potassium sulphate; the directly measured pressure at the pressure eutectic was 10,880 bars. Investigation of the system from 30°C. downwards has provided evidence[98] of the existence of potassium sulphate monohydrate, K_2SO_4,H_2O. The system has been further studied.[99]

K_2SO_4 - Li_2SO_4. The double compounds, $LiKSO_4$,[100] melting at[101] 716°C., and $2Li_2SO_4,K_2SO_4$, which melts at 550°C with decomposition,[102] are formed.

K_2SO_4 - Na_2SO_4. At temperatures close to fusion, the system forms a complete series of solid solutions.[100]

K_2SO_4 - K_2S. The double compound $K_2SO_4,3K_2S$, m.p. 755-9°C., is formed.[103]

K_2SO_4 - KCl. No compound formation was observed.[101]

K_2SO_4 - K_2CrO_4. An uninterrupted series of solid solutions is formed; between 585 and 666°C., the hexagonal (*α*) go over into the orthorhombic (*β*) solid solutions.[104]

K_2SO_4 - $ZnSO_4$. Two congruently fusing compounds, $ZnSO_4,K_2SO_4$, and $2ZnSO_4,K_2SO_4$, are formed.[105]

K_2SO_4 - $(NH_4)_2SO_4$. Complete solid solution has been observed.[100]

K_2SO_4 - V_2O_5. A compound of composition close to V_2O_5,K_2SO_4 and melting at approximately 500°C.has been detected.[106]

K_2SO_4 - H_2SO_4. The double compounds, $K_2SO_4,3H_2SO_4$, m.p. 91·5°C., and K_2SO_4,H_2SO_4, m.p. 218·6°C. have been observed;[107] the latter exists in three modifications with transition points at 182° and 202°C.

Data for the systems K_2SO_4 - KI and K_2SO_4 - KBr have been used to verify some rules relating to the determination of the type of phase diagrams of binary systems.[108] In the systems K_2SO_4 - $MgSO_4$ and K_2SO_4 - $ZnSO_4$ it has been shown that the end products obtained by crystallization from anhydrous melts are the same as the dehydration products of schönites.[109]

Many ternary aqueous systems in which potassium sulphate is one component, have been studied. Some of these systems, e. g. K_2SO_4 - Na_2SO_4 - H_2O and K_2SO_4 - $MgSO_4$ - H_2O, are of practical importance in the processing of natural sulphate solutions. Ternary aqueous systems were studied and the results obtained are summarized below.

K_2SO_4 - Li_2SO_4 - H_2O. At 25°C. there are[110] three solid phases, anhydrous potassium sulphate, lithium sulphate monohydrate, Li_2SO_4,H_2O, and solid solutions of the double salt, Li_2SO_4,K_2SO_4 with lithium sulphate; the limits of the molar ratio of K:Li in the solid solutions vary from 1:1 to 1:1·08.

K_2SO_4 - Na_2SO_4 - H_2O. At 25°C. there are[111] three solid phases, anhydrous potassium sulphate, sodium sulphate decahydrate, $Na_2SO_4,10H_2O$, and solid solutions of anhydrous sodium sulphate in glaserite, $3K_2SO_4,Na_2SO_4$. At 90°C., there are[111] three solid phases, anhydrous potassium sulphate, anhydrous sodium sulphate and solid solutions of anhydrous sodium sulphate in glaserite. Four solid phases can exist[112] over the temperature range 0-100°C.: anhydrous potassium sulphate, anhydrous sodium sulphate, sodium sulphate decahydrate, and glaserite. Glaserite and solid solutions of glaserite with anhydrous sodium sulphate are formed.[113] Indications of the formation of the double salt, $2Na_2SO_4,5K_2SO_4$, have been obtained.[114]

$K_2SO_4 - K_2CO_3 - H_2O$. Neither compounds nor solid solutions are formed.[115,116]

$K_2SO_4 - KHCO_3 - H_2O$. Neither compounds nor solid solutions are formed.[116]

$K_2SO_4 - KNO_3 - H_2O$. At both 25° and 90°C. neither hydrates nor double salts are formed.[111] At both 0° and 99·5°C. the results of Cornec and Hering have been confirmed.[117] The data for the system have been discussed[119] in relation to the separation of potassium nitrate and the recovery of other salts from crude Indian saltpetre. The depression of the melting point of the eutectic $K_2SO_4 - KNO_3$ - ice has been determined for a number of substances.[118]

$K_2SO_4 - KH_2PO_4 - H_2O$. From 30° to $-3·1$°C., neither solid solutions nor double salts are formed.[89]

$K_2SO_4 - KVO_3 - H_2O$. At 25°C. there is no compound formation.[120]

$K_2SO_4 - K_2CrO_7 - H_2O$. The system has been investigated[121] to determine whether the partition law is applicable to the equilibrium between a mixed crystal phase and the coexistent solution.

$K_2SO_4 - K_2Cr_2O_7 - H_2O$. From 20° to 40°C., neither hydrates nor double salts are formed.[122]

$K_2SO_4 - KSO_3NH_2 - H_2O$. At 25°C. the pure salts are the only solid phases.[123]

$K_2SO_4 - KCl - H_2O$. The effect of varying concentrations of ammonia on the system has been studied.[80]

$K_2SO_4 - KI - H_2O$. At 25°C. neither compounds nor solid solutions are formed.[124]

$K_2SO_4 - KClO_3 - H_2O$. No double salt is formed[125] at 15°, 25° or 45°C.

$K_2SO_4 - KBrO_3 - H_2O$. No double salt is formed[126] at 25°C.

$K_2SO_4 - KIO_3 - H_2O$. No double salt is formed[127] at 5°, 25° or 50°C.

$K_2SO_4 - K_4[Fe(CN)_6] - H_2O$. The system has been studied[128] from 0° to 90°C. and possible applications of the data indicated. Other data for the system have been applied[129] to the removal of potassium sulphate from technical potassium ferrocyanide.

$K_2SO_4 - K_2Mg(SO_4)_2 - H_2O$. The system has been investigated[130] between 0° and 63·4°C.

$K_2SO_4 - CuSO_4 - H_2O$. At 25°, 51° and 61°C. the hydrated double salt, $CuSO_4,K_2SO_4,6H_2O$, is formed;[131] it is stable for molar ratios of Cu:2K between 7:1 and 1:8. The system has been reinvestigated in part[132] and it was found that the maximum water content of the solubility curve does not occur in the pure aqueous solution of the double salt but in a solution containing excess of potassium sulphate.

$K_2SO_4 - MgSO_4 - H_2O$. At[117] 0° and at[133] 30°C. there are three solid phases, anhydrous potassium sulphate, magnesium sulphate heptahydrate, $MgSO_4,7H_2O$, and schönite. At 30°C. mixed crystals are not formed.[133] At 85°C. there are[134] four solid phases, anhydrous potassium sulphate, leonite, langbeinite and kieserite. At[117] 99·5°C. and at[134] 100°C. there are three solid phases, anhydrous potassium sulphate, langbeinite and kieserite. From the equilibria of the system at 35° and 100°C., a plan of fractional crystallization has been worked out[135] to give pure anhydrous potassium sulphate starting from a solution containing potassium and magnesium sulphates. The solubility data on the system have been studied[136] in the light of a solubility equation.[137] The system has been investigated[138] by adding methyl alcohol to the solution. Additional data for the system have been obtained[139] and further analysed.[140]

K_2SO_4 - $CuSO_4$ - H_2O. At 40°C. the solid phases are[141] anhydrous potassium sulphate, gypsum, the pentasalt, $K_2SO_4,5CaSO_4,H_2O$ and syngenite, $K_2SO_4,CaSO_4,H_2O$. At 55°C. the solid phases are[142] anhydrous potassium sulphate, anhydrous calcium sulphate, the pentasalt, and syngenite. At 60° and 100°C., the solid phases are[141] anhydrous potassium sulphate, anhydrous calcium sulphate, gypsum, the pentasalt and syngenite. The equilibrium concentration of potassium sulphate in solution at 100°C for the equations:-

$$5(CaSO_4,2H_2O) + K_2SO_4 = K_2SO_4,5CaSO_4,H_2O + 9H_2O$$

and

$$K_2SO_4,5CaSO_4,H_2O + 4K_2SO_4 + 4H_2O \rightleftharpoons 5(K_2SO_4,CaSO_4,H_2O)$$

has been determined.[143]

K_2SO_4 - $ZnSO_4$ - H_2O. The range of existence of the double salt is[144] 0·19 to 21·3 moles of zinc sulphate to 1 mole of potassium sulphate.

K_2SO_4 - $CdSO_4$ - H_2O. At 25°C., the addition of potassium sulphate to a saturated solution of cadmium sulphate causes the separation of the double salt, $CdSO_4,K_2SO_4$.[145] The following double salts have been observed:-[146] $CdSO_4,K_2SO_4,4H_2O$; $CdSO_4,K_2SO_4,1{\cdot}5H_2O$; $3CdSO_4,K_2SO_4,5H_2O$; $3CdSO_4,K_2SO_4,2H_2O$; $3CdSO_4,2K_2SO_4,H_2O$.

K_2SO_4 - $Al_2(SO_4)_3$ - H_2O. At 25°C., there are[147] three solid phases, anhydrous potassium sulphate, anhydrous aluminium sulphate and potash alum. Potash alum exists as a solid phase at 0 °C.[148]

K_2SO_4 - $La_2(SO_4)_3$ - H_2O. At 25°C., the following compounds have been observed:-[149] $2La_2(SO_4)_3,3K_2SO_4,8H_2O$; $La_2(SO_4)_3,4K_2SO_4,H_2O$; $La_2(SO_4)_3,4{\cdot}5K_2SO_4,2H_2O$; $La_2(SO_4)_3,5K_2SO_4,2H_2O$.

K_2SO_4 - $Ce_2(SO_4)_3$ - H_2O. At 25°C., the following compounds have been identified:-[150] $Ce_2(SO_4)_3,5K_2SO_4$; $Ce_2(SO_4)_3,4{\cdot}5K_2SO_4$; $2Ce_2(SO_4)_3,3K_2SO_4,8H_2O$; $Ce_2(SO_4)_3,K_2SO_4,2H_2O$; the results are compared with those of earlier investigations.

K_2SO_4 - $Nd_2(SO_4)_3$ - H_2O. At 25°C., the following compounds are formed:-[149]

$$Nd_2(SO_4)_3,K_2SO_4,2H_2O;\quad Nd_2(SO_4)_3,3K_2SO_4,2H_2O;$$
$$Nd_2(SO_4)_3,4K_2SO_4,H_2O;\quad Nd_2(SO_4)_3 4K_2SO_4,2H_2O;$$
$$Nd_2(SO_4)_3,5K_2SO_4,2H_2O;\quad 2Nd_2(SO_4)_3,3K_2SO_4,8H_2O.$$

K_2SO_4 - Tl_2SO_4 - H_2O. At 25°C., continuous solid solutions are formed[132] between potassium and thallous sulphates.

K_2SO_4 - $(NH_4)_2SO_4$ - H_2O. From 0° to 96·5°C.,[151] from the temperature of complete solidification to 30°C.,[152] at 25°C.[153] and at 30°C.,[154] the two salts form continuous solid solutions.

K_2SO_4 - $Bi_2(SO_4)_3$ - H_2O. At 25°C., the double salt, $Bi_2(SO_4)_3,3K_2SO_4$, is formed;[155] it is stable in solutions containing 5·32 to 12·8% of potassium sulphate.

K_2SO_4 - UO_2SO_4 - H_2O. The system has been studied[156] at 25°C.

K_2SO_4 - $MnSO_4$ - H_2O. At[157],[158] 0° and at[157] 25°C., the hydrated double salt, $MnK_2(SO_4)_2,4H_2O$ is formed; at 25°C., the range of existence of the double salt is[144] 1·5 to 10·4 moles of manganous sulphate to 1 mole of potassium sulphate.

K_2SO_4 - $CoSO_4$ - H_2O. At 25°C., the hydrated double salt $CoSO_4,K_2SO_4,6H_2O$, is formed.[159] The system has been further studied.[160]

K_2SO_4 - $NiSO_4$ - H_2O. At 25°C., the range of existence of the double salt is[144] 0·031 to 3·8 moles of nickel sulphate to 1 mole of potassium sulphate. The system has been further studied.[160]

K_2SO_4 - H_3BO_3 - H_2O. From 2° to 25°C.[161] and from 25° to 100°C.[162] neither compounds nor solid solutions are formed.

K_2SO_4 - H_2SO_4 - H_2O. At 30°, 50° and 75°C., the double salts, $K_2SO_4,3KHSO_4$ and $K_2SO_4,6KHSO_4$ are formed;[163] the system has been further studied.[164]

K_2SO_4 - sucrose - H_2O. At 30°C., no compound is formed.[165]

K_2SO_4 - dextrose - H_2O. At 30°C., no compound is formed.[166]

K_2SO_4 - urea - H_2O. The system has been studied[167] from −13° to 25°C.

The equilibria in a number of quaternary aqueous systems containing reciprocal salt pairs have been investigated. The systems studied and the results obtained are given below.

K_2SO_4 - Na_2SO_4 - KNO_3 - $NaNO_3$ - H_2O. At 90°C., the solid phases are[111,112,168] anhydrous potassium sulphate, anhydrous sodium sulphate, anhydrous potassium nitrate, anhydrous sodium nitrate, and glaserite. At 74°C., darapskite, $Na_2SO_4,NaNO_3,H_2O$, is formed.[112,168]

At 32·4°C., sodium sulphate decahydrate, $Na_2SO_4,10H_2O$, appears.[168,169] At 25°C., there is a new solid of unknown composition[111] the existence of which could not be confirmed.[169] At 21·8°C., anhydrous sodium sulphate disappears,[169] and at 10°C. darapskite disappears.[169] At −2°C., the solid phases are[169] anhydrous potassium sulphate, anhydrous potassium nitrate, glaserite and sodium sulphate decahydrate. The results have been discussed[119] in relation to the separation of potassium nitrate and the recovery of other salts from crude Indian saltpetre.

K_2SO_4 - Na_2SO_4 - K_2CO_3 - Na_2CO_3 - H_2O. At 25°C. the solid phases are[170] anhydrous potassium sulphate, the hydrates of sodium carbonate, sodium sulphate decahydrate and glaserite.

K_2SO_4 - Na_2SO_4 - KCl - $NaCl$ - H_2O. The effect of varying concentrations of ammonia on the system has been studied;[80] with increase in ammonia content, sodium sulphate decahydrate tends to disappear and glaserite tends to form. The system has been used[171] to illustrate a graphical method of representation for reciprocal salt-pair systems, and data for the system have been discussed.[172]

K_2SO_4 - $MgSO_4$ - KCl - $MgCl_2$ - H_2O. The system has been investigated[173] at 25°C. in order to study the formation of kainite and related salts; the data confirm the assumption that primary kainite can be deposited from marine brines. The system has been investigated at 15°, 25°, 35° and 55°C. with and without sodium chloride as saturating phase[174] and at 25°C. in the presence of sodium chloride;[173] the importance of the presence of the data in the technical utilization of sulphate-containing solutions has been discussed.[174]

K_2SO_4 - $MgSO_4$ - KNO_3 - $Mg(NO_3)_2$ - H_2O. The system has been investigated[175,176] between 0° and 100°C.

K_2SO_4 - $CaSO_4$ - KCl - $CaCl_2$ - H_2O. At 25°C., the solid phases are[177] anhydrous potassium sulphate, anhydrous potassium chloride, calcium chloride hexahydrate, $CaCl_2,6H_2O$, calcium sulphate dihydrate, $CaSO_4,2H_2O$, and syngenite, $K_2SO_4,CaSO_4,H_2O$. At 55°C. the solid phases are[142] anhydrous potassium sulphate, anhydrous potassium chloride, anhydrous calcium sulphate, calcium chloride dihydrate, $CaCl_2,2H_2O$, the double salt, $KCl,CaCl_2$, the pentasalt, $K_2SO_4,5CaSO_4,H_2O$, and syngenite. The data have been discussed[178] in relation to the formation of calcium chloride in natural brines. The system has been investigated in the presence of various concentrations of dissolved ammonia and it was shown that for the equilibrium at constant temperature and constant ammonia concentration, between potassium and calcium ions and the solids syngenite and potassium sulphate, the standard free enthalpy change is constant.[179]

K_2SO_4-$(NH_4)_2SO_4$-KNO_3-NH_4NO_3-H_2O. At 25°C. the solid phases are[180] all solid solutions of a number of different types. Investigation of the system at 0°, 25° and 50°C. has shown[181] the existence of another series of solid solutions.

K_2SO_4 - $(NH_4)_2SO_4$ - K_2CrO_4 - $(NH_4)_2CrO_4$ - H_2O. At 25°C., there are[182] two complete series of solid solutions.

K_2SO_4 - $(NH_4)_2SO_4$ - KSO_3NH_2 - $NH_4SO_3NH_2$ - H_2O. At 25°C. the solid phases are[123] one continuous solid solution of the sulphates and two series of solid solutions of the sulphamates.

K_2SO_4 - $CoSO_4$ - KCl - $CoCl_2$ - H_2O. The solid phases are[183] anhydrous potassium sulphate, anhydrous potassium chloride, cobalt chloride hexahydrate, $CoCl_2,6H_2O$, cobalt sulphate heptahydrate, $CoSO_4,7H_2O$ and the hydrated double salt, $K_2SO_4,CoSO_4,6H_2O$.

The following quaternary aqueous systems which do not contain reciprocal salt pairs have been investigated.

K_2SO_4 - Na_2SO_4 - $MgSO_4$ - H_2O. Solubility data for the system from 0° to 120°C. have been collected and correlated.[184]

K_2SO_4 - Na_2SO_4 - $(NH_4)_2SO_4$ - H_2O. The system has been investigated[185] at 60°C.

K_2SO_4 - KCl - KNO_3 - H_2O. At 25°C., the only solid phases are[186] single salts.

K_2SO_4 - $CuSO_4$ - Tl_2SO_4 - H_2O. At 25°C., the solid phases are[132] copper sulphate pentahydrate, $CuSO_4,5H_2O$, a continuous anhydrous solid solution of potassium and thallous sulphates and a continuous hydrated solid solution of two double salts, one congruently and one incongruently soluble.

K_2SO_4 - $MgSO_4$ - $CaSO_4$ - H_2O. The tentative stability fields at 100°C. for syngenite, $K_2SO_4,CaSO_4,H_2O$, polyhalite, $K_2SO_4,MgSO_4,2CaSO_4,2H_2O$, anhydrite, $CaSO_4$, and the pentasalt, $K_2SO_4,5CaSO_4,H_2O$, have been defined.[187]

K_2SO_4 - $MgSO_4$ - H_3BO_3 - H_2O. At 0°C., the solid phases are[139] boric acid, anhydrous potassium sulphate, magnesium sulphate hexahydrate, $MgSO_4,6H_2O$, and magnesium sulphate dodecahydrate, $MgSO_4,12H_2O$; at 15° and 25°C., the dodecahydrate is replaced by the heptahydrate, $MgSO_4,7H_2O$.

The following multicomponent aqueous systems containing potassium sulphate have been investigated.

K_2SO_4 - $NaCl$ - $MgSO_4$ - H_2O. The solid phases are[188] at 25°C., schönite, $MgSO_4,K_2SO_4,6H_2O$, magnesium sulphate heptahydrate, $MgSO_4,7H_2O$, and astrakanite, $MgSO_4,Na_2SO_4,4H_2O$, at 55°C., leonite, $MgSO_4,K_2SO_4,4H_2O$, magnesium sulphate hexahydrate, $MgSO_4,6H_2O$, and löweite, $MgSO_4,Na_2SO_4,2{\cdot}5H_2O$ and at 83°C., leonite, langbeinite, $2MgSO_4,K_2SO_4$, and löweite.

K_2SO_4 - Na_2SO_4 - KCl - $NaCl$ - KNO_3 - $NaNO_3$ - H_2O. At 75°C., the solid phases are[112] the six single salts and glaserite; the system has been further investigated[189] from 0° to 90°C.

The solubility equilibria in some multicomponent aqueous systems containing potassium sulphate have been considered[190] in relation to the solar evaporation of sea water; the solid contents of sea water under varying conditions have been extensively studied.[191]

Non-aqueous systems containing more than two components which have been studied are:-

$K_2SO_4 - Li_2SO_4 - KNO_3 - LiNO_3$;[52] $K_2SO_4 - Li_2SO_4 - K_2WO_4 - Li_2WO_4$;[192]
$K_2SO_4 - Na_2SO_4 - KCl - NaCl$;[193] $K_2SO_4 - Na_2SO_4 - KNO_3 - NaNO_3$;[194]
$K_2SO_4 - Na_2SO_4 - KOH - NaOH$;[195] $K_2SO_4 - Rb_2SO_4 - KCl - RbCl$;[101]
$K_2SO_4 - Cs_2SO_4 - KCl - CsCl$;[101] $K_2SO_4 - MgSO_4 - KNO_3 - Mg(NO_3)_2$;[196]
$K_2SO_4 - CaSO_4 - KCl - CaCl_2$;[197] $K_2SO_4 - PbSO_4 - K_2WO_4 - PbWO_4$;[198]
$K_2SO_4 - (NH_4)_2SO_4 - KNO_3 - NH_4NO_3$;[199,200] $K_2SO_4 - CoSO_4 - KCl - CoCl_2$;[201]
$K_2SO_4 - Li_2SO_4 - Na_2SO_4$;[102] $K_2SO_4 - Na_2SO_4 - CuSO_4$;[202,203]
$K_2SO_4 - Na_2SO_4 - MgSO_4$;[204] $K_2SO_4 - KCl - (NH_4)_2Cr_2O_7$;[205]
$K_2SO_4 - KNO_3 - K_2CrO_4$;[104] (K,Li) ($SO_4$,Cl,$WO_4$);[206]
(K,Na,Mg) (SO_4,Cl);[207,208] (K,Na,Zn) (SO_4,Cl);[209] (K,Na,Tl) (SO_4,Cl,NO_3).[207]

Various syntheses have been carried out to verify the reactions which take place between solid oceanic salts.[210]

The specific gravity of saturated aqueous solutions of potassium sulphate is[64] 1·0757 at 15°C., 1·0807 at 20°C. and 1·0853 at 25°C. The specific gravities at 25°C. of potassium sulphate solutions of various concentrations[86] are given in Table VII and the densities from 20° to 90°C. of a solution containing 10·962 g. of potassium sulphate in 100 c.c. of solution[211] are given in Table VIII.

TABLE VII.- SPECIFIC GRAVITY OF POTASSIUM SULPHATE SOLUTIONS AT 25°C.

Normality of soln.	Specific gravity
0·088	1·0033
0·348	1·0212
0·527	1·0335
0·810	1·0520
1·103	1·0712
1·340	1·0864

TABLE VII.- DENSITY OF POTASSIUM SULPHATE SOLUTION FROM 20° TO 90°C.
(10·962 g. K_2SO_4 per 100 c.c. of solution)

t°C.	Density
20	1·0817
30	1·0784
40	1·0746
50	1·0702
60	1·0653
70	1·0599
80	1·0541
90	1·0481

The specific gravity has also been determined for 0·1 to 1·0N solutions[212] from 10° to 50°C., and for 0·1 and 0·5 molar solutions.[213] The density of solutions containing a mixture of potassium and zinc sulphates at 0·1 and 0·5 total molar concentrations have been measured;[213] for 0·1 molar solutions, the densities agree with the values calculated by the law of mixtures but for 0·5 molar solutions the experimental values are higher than the calculated.

Mendelēev's characteristic temperature, the temperature at which the coefficient of thermal expansion of a solution becomes equal to that of water, is[214] of the order of 50°C. for potassium sulphate solutions.

The diffusion coefficients for aqueous diffusion of potassium sulphate from 19° to 25°C. have been determined;[215] the activation energy of free diffusion is 3,700 g.-cal. per mole. The Soret coefficient of a 0·1N solution of potassium sulphate is[216] $17 \cdot 1 \times 10^{-3}$ degree^{-1} for a cellophane membrane and $11 \cdot 4 \times 10^{-3}$ degree^{-1} for an ultra-fine filter. Diffusion coefficients at 0°, 25° and 50°C. have been measured[217] as a function of pressure for the diffusion of ^{35}S-tagged 0·1N-potassium sulphate solution into untagged 0·1N-potassium sulphate solution; the diffusion coefficients at 0°C. are given in Table IX.

TABLE IX.- DIFFUSION COEFFICIENTS (D) FOR 0·1 N-POTASSIUM SULPHATE SOLUTION AT 0°C. AND VARIOUS PRESSURES (P)

P (atm.)	$D \times 10^5$ (cm.^{2}/sec.)
10	0·33
100	0·67
265	0·71
390	0·50
415	0·40
600	0·90
775	0·86
1060	0·83
1800	0·82
3075	0·66

The diffusion constant of potassium sulphate in agar gel has been determined[218] from 10° to 20°C. The diffusion of potassium sulphate into gelatin solutions containing barium chloride has been studied.[219] Experiments in which solutions of potassium sulphate and barium chloride were allowed to diffuse towards each other through a thin sheet of gelatin have been used[220] to study steady-state diffusion systems determined by mutual precipitation of two reagents. The diffusion of a mixture of potassium sulphate and potassium chloride in agar gel has been studied.[218]

The viscosity of aqueous solutions of potassium sulphate has been measured.[211,212,213,221] The relative viscosity of potassium sulphate solutions is almost proportional to the concentration.[212] The fluidity data given in Table X agree well with the formula of Meyer and Rosencranz.

TABLE X.- FLUIDITY OF POTASSIUM SULPHATE SOLUTION FROM 20°TO 90°C.
(10·962 g. K_2SO_4 per 100 c.c. of solution)

t°C.	Fluidity
20	88·0
30	107·1
40	129·7
50	154·2
60	175·2
70	199·7
90	247·6

The relative viscosities[221] from 25° to 85°C. of 0·01 to 0·30N-potassium sulphate solutions are given in Table XI; the results confirm the predictions of the Debye–Hückel theory.

TABLE XI. RELATIVE VISCOSITY OF POTASSIUM SULPHATE SOLUTIONS FROM 25° TO 85°C.

t°C.	Normality of solution at 25°C.				
	0·0100	0·0500	0·1001	0·2000	0·3000
25	1·0029	1·0126	1·0244	1·0450	1·0685
30	1·0033	1·0131	1·0258	1·0486	1·0736
35	1·0035	1·0136	1·0271	1·0517	1·0779
40	1·0036	1·0141	1·0287	1·0542	1·0816
45	1·0038	1·0150	1·0301	1·0563	1·0850
50	1·0037	1·0160	1·0311	1·0580	1·0878
55	1·0038	1·0166	1·0320	1·0597	1·0909
60	1·0040	1·0168	1·0327	1·0613	1·0934
65	1·0041	1·0172	1·0333	1·0630	1·0953
70	1·0043	1·0175	1·0341	1·0646	1·0976
75	1·0044	1·0181	1·0350	1·0660	1·0989
80	1·0046	1·0187	1·0354	1·0676	1·1002
85	1·0049	1·0187	1·0361	1·0683	1·1022

In 0·1N-potassium sulphate solution, the specific ionic viscosity of potassium ions is[78] −0·0030 and that of sulphate ions is 0·0135. The viscosity of solutions containing a mixture of potassium and zinc sulphates has been measured.[213] A rule for calculating the dynamic viscosity of aqueous solutions containing three or four electrolytes has been illustrated[222] using data for potassium sulphate. Potassium sulphate has much less effect on the viscosity of aqueous sucrose solutions than have acetates or carbonates.[223]

Compression measurements on aqueous solutions of potassium sulphate at 25°C. showed an increase in the fictive (partial) volume of potassium sulphate.[76] The adiabatic compressibility of aqueous potassium sulphate solutions has been determined at 30°C. and the results discussed in relation to ionic hydration.[224]

The surface tension of potassium sulphate solutions at 25°C. has been determined;[225] below a certain concentration, the surface tension of the solution is less than that of water while above that concentration the surface tension increases and is an approximately linear function of the concentration. Data for potassium sulphate and lithium carbonate in the presence of various capillary-active compounds[226] show that a salt which raises the surface tension of water decreases the solubility of a non-conductor in the salt solution whereas a salt which lowers the surface tension of water increases the solubility of the non-conductor.

The boiling point of a saturated aqueous solution of potassium sulphate has been measured.[227]

The vapour pressures of saturated aqueous solutions of potassium sulphate have been measured[228] between 0° and 25°C.; the variation of vapour pressure (p) with temperature (T) can be represented by the equation:-

$$\log p = -2332{\cdot}5/T + 9{\cdot}1881$$

The vapour pressures from 20° to 50°C. of saturated aqueous solutions of potassium sulphate[229] are given in Table XII.

The vapour pressures at 30·01°C. of potassium sulphate solutions of various concentrations[230] are given in Table XIII.

Potassium sulphate solution has been used to test an apparatus for the measurement of vapour pressure.[231] The vapour pressure of saturated solutions of potassium sulphate and of mixtures of potassium sulphate with other salts has been measured.[227]

TABLE XII.- VAPOUR PRESSURE (p) FROM 20° TO 50 °C. OF SATURATED AQUEOUS POTASSIUM SULPHATE SOLUTION

t°C.	Molality of soln.	p (mm. Hg)
18·90	0·6256	15·91
22·25	0·6620	19·55
24·73	0·6884	22·60
25·58	0·6974	23·89
31·55	0·7600	33·61
35·96	0·8052	42·90
43·42	0·8825	63·74
48·41	0·9333	82·11
52·30	0·972	99·13

TABLE XIII.- VAPOUR PRESSURE (p) AT 30·01°C. OF POTASSIUM SULPHATE SOLUTIONS

(concentrations in grams of K_2SO_4 per 100 g. of water)

Concentration	p (mm. Hg)
0·93	31·64
1·78	31·60
3·28	31·49
5·43	31·38
7·33	31·23
7·82	31·22
13·04	30·89

The variation of relative humidity with temperature has been determined[232] in air in equilibrium with saturated solutions of potassium sulphate from 0° to 50°C. The Magnus formula for the variation of the vapour pressure of water with temperature applies also to concentrated solutions of potassium sulphate.[233] A relation for the lowering of the vapour pressure has been verified[234] for aqueous solutions of potassium sulphate at 30° and 80°C. The effect of saturated potassium sulphate solution on the vapour-liquid equilibrium of the water-ethyl alcohol system has been investigated.[235] The freezing point data for 0·001 to 0·01 molal aqueous solutions of potassium sulphate given in Table XIV agree well with values calculated from the formula of Debye and Hückel.[236]

TABLE XIV.- FREEZING POINT LOWERING FOR AQUEOUS POTASSIUM SULPHATE SOLUTIONS

Molality of soln.	F.p. lowering
0·001	0·00526
0·00274	0·00530
0·005	0·02565
0·01	0·05005

The lowering of the freezing point has been measured[237] for aqueous potassium sulphate solutions at several concentrations between 0·0031 and 0·4074 molal, and for dilute aqueous solutions of equimolar mixtures of potassium sulphate, potassium nitrate, magnesium sulphate, and calcium nitrate.[238] A theoretically developed relation between the abnormal lowering of the freezing point for electrolytes and the increase in surface tension gives good agreement with experiment for potassium sulphate and other electrolytes.[239] The freezing points of solutions of various concentrations of potassium sulphate in 98%

hydrogen peroxide[240] are given in Table XV.

TABLE XV. FREEZING POINT OF SOLUTIONS OF POTASSIUM SULPHATE IN 98% HYDROGEN PEROXIDE

Mole % of K_2SO_4	F.p. °C.
0·87	−2·0 H_2O_2 solid phase
2·27	−4·8
3·68	−8·2
5·3	−12·3
7·6	−17·5
8·4	−23·5
14·1	−11·0 K_2SO_4 solid phase
15·9	+0·5

The freezing point lowering for solutions of potassium sulphate in anhydrous sulphuric acid has been determined;[247] the freezing point constant is 5·97 deg. g.-mol^{-1} kg. The freezing point depression for solutions of potassium sulphate in nitrobenzene is[242] 0·506°C. for a solution containing 0·432 moles of potassium sulphate in 100 moles of solution and 0·504°C. for a solution containing 0·795 moles of potassium sulphate in 100 moles of solution.

Osmotic coefficients for potassium sulphate and other electrolytes have been determined[238] from measurements of the lowering of the freezing point of dilute solutions of mixtures of two of the electrolytes; the experimental values are in fair agreement with those calculated by means of the Debye-Hückel theory. The velocity constant of permeation of potassium sulphate through a semipermeable membrane has been determined.[243] The absorption of potassium sulphate from solution during contact with copper ferrocyanide has been investigated.[244] The specific heats of aqueous potassium sulphate solutions utions[245] at various temperatures are given in Table XVI.

TABLE XVI. SPECIFIC HEAT OF AQUEOUS POTASSIUM SULPHATE SOLUTIONS

t°C.	Molality of soln.	Specific heat
21	10·34	0·8934 ± 0·0001
41	8·0	0·9067 ± 0·004
86	10·36	0·9043 ± 0·005

The apparent molal volume of glycine has been measured[246] in potassium sulphate solutions of various concentrations.

The refractive index for the sodium D line of a saturated solution of potassium sulphate is[64] 1·34470 at 15°C., 1·34507 at 20°C. and 1·4537 at 25°C.

The electrical conductivities of potassium sulphate solutions from 18° to 85°C. for[247] 0·001 to 0·1N solutions and for[248] 0·0005N solutions are given in Table XVII; even in dilute solutions the results are not in agreement with the Debye-Hückel-Onsager theory.

At 25°C., the conductivity of 0·00208 molal aqueous potassium sulphate solution is[237] 0·000583 and that of 0·41708 molal solution is 0·069278. The effect of pressure on the conductivity of dilute aqueous potassium sulphate solutions has been investigated[249] at 25°C.; the relative resistance (the ratio of the resistance, R, of the cell at the given pressure to the resistance, R_0, at atmospheric pressure) is given in Table XVIII for a 1·6861% solution; similar measurements have been made on 0·1739% and 0·4336% solutions. Other measurements under pressure have shown[250] that the relative resistance depends to some extent on the concentration.

The high frequency conductivity of potassium sulphate solution at[251] a wave-length of 3 metres, and at[252] a frequency of $4{\cdot}39 \times 10^7$ hertz have been measured; the conductivity at high frequency is not significantly different from that at low or medium frequencies.[251,252]

The conductivity of dilute potassium sulphate solutions at large high-frequency field strengths has been investigated.[253]

TABLE XVII. EQUIVALENT CONDUCTIVITY OF AQUEOUS POTASSIUM SULPHATE SOLUTIONS FROM 18° TO 85°C.

t°C	Normality of Solution						
	0·1 (approx.)	0·05	0·02	0·01	0·005	0·001	0·0005
18	94·8	101·68	110·1	115·9	120·1	126·7	128·5
25	109·7	118·0	128·1	134·2	139·4	148·0	150·2
30	120·7	129·8	141·5	148·1	153·7	165·8	167·8
35	131·8	140·8	155·1	163·3	168·9	183·6	187·5
40	143·1	153·2	168·8	179·1	185·0	200·0	204·8
45	154·7	166·5	182·5	194·2	202·3	218·3	224·1
50	166·0	180·1	196·2	210·1	218·1	236·7	242·3
55	177·9	193·4	210·1	226·5	232·7	252·5	260·8
60	189·8	207·0	224·2	239·8	249·7	269·7	278·5
65	201·9	220·4	239·2	258·4	265·8	286·2	297·7
70	214·0	234·4	253·5	273·6	282·0	307·6	318·1
75	226·4	248·4	269·5	291·0	300·6	327·3	337·4
80	238·9	262·5	284·8	308·2	317·5	346·2	356·3
85	251·4	276·6	301·3	324·6	336·5	367·2	375·6

TABLE XVIII.- CONDUCTIVITY OF A 1·6861% POTASSIUM SULPHATE SOLUTION UNDER PRESSURE (P) AT 25°C.

P (bars)	R/R_0
1	1·00000
583	0·94913
1055	0·92227
1368	0·90896
1633	0·90136
1885	0·89540
2145	0·89084
2606	0·88634
2941	0·88516
3128	0·88565
3691	0·88952

The conductivity of a solution containing a mixture of potassium and sodium sulphates and of a solution containing a mixture of potassium and magnesium sulphates has been studied[254] in order to determine whether double salts are formed. The conductivity of potassium sulphate in aqueous solutions of sucrose has been measured,[255,256] as has the conductivity of potassium sulphate in 2% agar sol and in 2% agar gel.[257]

The equivalent conductivity of hydrogen fluoride solutions of potassium sulphate is[83] of the order of 200×10^{-4} mho.

The variation of conductivity of solid potassium sulphate with temperature has been measured[258] at high temperatures.

At 18°C. the dissociation constants of potassium sulphate are[259] 1·5 for the equilibrium $[K^+]\,[KSO_4^-]\ /\ [K_2SO_4]$ and 2×10^{-2} for the equilibrium $[K^+]\,[SO_4^{2-}]\ /\ [KSO_4^-]$.

The percentage ionisation of potassium sulphate has been calculated thermodynamically from freezing point data,[260] with the results given in Table XIX.

TABLE XIX.- DISSOCIATION OF POTASSIUM SULPHATE IN AQUEOUS SOLUTION

Molal concn.	% Ionisation
10^{-2}	68·7
10^{-3}	85·3
10^{-4}	93·5
10^{-5}	97·2
10^{-6}	98·8
10^{-7}	99·5

The degree of dissociation of potassium sulphate has been calculated from conductivity data by using the Onsager theory and assuming an intermediate ion;[261] the dissociation constant of the KSO_4^- ion is 0·151. The dissociation constant of a mixture of potassium sulphate solution and an acid moor soil has been calculated from measurements of the hydrogen ion concentration and the titration of a potassium sulphate extract of the soil.[262] The lowering of the eutectic point of ice and potassium sulphate by the addition of a salt with one common ion has been explained in terms of the dissociation of the added salt.[263]

The activity coefficient of potassium sulphate in aqueous solution as calculated from freezing point data is[264] 0·889 for a 0·001 molar solution, 0·781 for a 0·005 molar solution and 0·715 for a 0·01 molar solution; the activity coefficients in aqueous solution have also been calculated from e.m.f. measurements[265,266,267] and are given in Table XX for various molarities[265] and molalities.[266]

TABLE XX. ACTIVITY COEFFICIENT (γ) OF POTASSIUM SULPHATE IN AQUEOUS SOLUTION

Molarity of soln.	γ	Molality of soln.	γ
0·025	0·597	0·025	0·602
0·050	0·500	0·050	0·504
0·125	0·373	0·125	0·376
0·248	0·297	0·248	0·299
0·494	0·238	0·494	0·240
0·621	0·218	0·621	0·220

From experimental activity data, the sum of the ionic radii of potassium sulphate has been calculated[268] as 3·8A. The activities of water in potassium sulphate solutions,[265,266] of sulphuric acid in potassium sulphate solutions[265,266,269] and of potassium hydroxide in potassium sulphate solutions[265,266] have been computed from e.m.f. measurements. Ionic activities in potassium sulphate solution have been measured with an electrode containing a membrane of Zeo-Carb 315 resin.[270] The mean activity coefficient of potassium sulphate in a sulphonated styrene–divinylbenzene resin has been determined.[271]

From transport number measurements in 0·0025 to 0·5N potassium sulphate solutions, the transport number extrapolated to infinite dilution is[272] 0·477 at 25°C. Calculated cation transport numbers of potassium sulphate[261] are given in Table XXI; the calculated values agree well with the experimental values.

The transport numbers in various membranes for potassium sulphate have been determined[273] from e.m.f. measurements. The relation of ionic mobility to charge has been investigated[274] for potassium sulphate solutions. The calculated mobility of the ion, KSO_4^-, is[259] 115.

TABLE XXI.- CATION TRANSPORT NUMBER OF POTASSIUM SULPHATE

Equiv. Concn.	Cation Transport No.
0·0	0·487
0·01	0·492
0·02	0·492
0·05	0·492
0·1	0·492
0·2	0·491

The dielectric constant of potassium sulphate solutions has been measured[275] at 23°C. and 2 × 10^6 cycles frequency; the increase in dielectric constant with concentration is greater than that predicted by the theory of Debye and Falkenhagen. The electrode potential of manganese at 25°C. in potassium sulphate solutions is independent of the concentration of potassium sulphate.[276] The electrode potentials of electrolytically polished aluminium, iron, nickel, copper, and tungsten in potassium sulphate solution are higher than those of the unpolished metals owing to the coating of oxide films on the electrolytically polished surfaces.[277] The variation in pH that occurs as 0·5N-barium nitrate or lead nitrate solution is added to 1N-potassium sulphate solution has been determined potentiometrically;[278] the results are explained in terms of hydrolytic adsorption and ionic exchange during the course of the precipitation. The changes in pH that occur as 0·1 molar barium chloride solution is added to 0·1 molar potassium sulphate solution, and as potassium sulphate solution is added to barium chloride solution, have been determined and interpreted in terms of adsorption or desorption of hydrogen or hydroxyl ions on the surface of the precipitates.[279] The changes in pH that occur as tungstate solutions are added to dilute aqueous solutions of potassium sulphate have been investigated potentiometrically.[280] The electrical resistance of permselective collodion membranes in potassium sulphate solutions has been studied.[281] The potential ratio between electrodes of charged (500-600 V.) blotting paper, and the variation of potential between points on the electrode, have been measured[282] with the electrodes dipping into aqueous solutions of potassium sulphate; the potential shows an increase at the cathode.

Potassium sulphate accelerates the velocity of solution of aluminium in 1·4N-hydrochloric acid at 25°C.[283] Yeast fermentation is accelerated about 25% in 0·2N-potassium sulphate solution.[284] The effect of potassium sulphate and of a mixture of potassium and ferrous sulphates, used as catalysts in the crystallization of gypsum from aqueous solution, on the crystalline form of the gypsum has been investigated.[285] Potassium sulphate promotes the catalytic activity of aluminium oxide in the preparation of butadiene from a mixture of ethyl alcohol and acetaldehyde[286] and also promotes the catalytic activity of vanadium pentoxide in the preparation of phthalic anhydride from phenanthrene.[287] The efficiency of vanadium pentoxide–potassium sulphate–silica gel as a catalyst in the oxidation of propane has been studied.[288] The crystalline state of potassium sulphate, present in a vanadium pentoxide catalyst, has been investigated and found to have very little effect on the activity of the catalyst.[289]

The effect of potassium sulphate on the rate of solution of gold in cyanide solutions,[290] on the quantity of soluble hydroxide required for the complete precipitation of hydrated stannic oxide from stannic chloride,[291] on the mutarotation and final rotation values of glucose,[292] on the optical properties of sulfonecyanine[293] and on the quenching of the fluorescence of the doubly positive ion of quinine by bromide ion and of the doubly negative ion of fluorescein by iodide ion[294] has been investigated. The corrosion of mild steel strip in dilute potassium sulphate solution has been studied.[295] The action of a mixture of sulphur dioxide, air and steam on potassium chloride, present as a mixture of potassium chloride, potassium sulphate and ferric oxide catalyst, has been investigated.[296]

The dialytical coefficient of potassium sulphate in 0·1N-aqueous solution is 0·574 for a cellophane membrane;[297] the dialysis of solutions of potassium sulphate has been further studied.[298] The differential capacity of the electrical double layer at a mercury-solution interface has been determined[299] at 25°C. for a 0·1N solution of potassium sulphate. The rate of change with concentration of the capacity of the electrical double layer on mercury has been measured[300] for potassium sulphate solutions. The zeta-potentials at a cellulose interface[301] for aqueous potassium sulphate solutions over a concentration range up to approximately 0·001N are given in Table XXII.

TABLE XXII. ZETA-POTENTIAL AT A CELLULOSE INTERFACE FOR AQUEOUS POTASSIUM SULPHATE SOLUTION

Normality × 10^3	ζ-potential (mV.)
0·0	−9·63
0·1	−12·16
0·2	−12·80
0·4	−11·39
0·8	−11·10

The zeta-potential of fluorspar has been measured[302] against potassium sulphate solutions of concentrations up to 0·01 molar; the potential is −23 mV. in pure water and increases to about −27 mV. in 0·01 molar potassium sulphate solution. The surface conductivity of potassium sulphate solutions at a boundary of Pyrex glass[303] and at a cellulose interface[301] has been measured; the absolute surface conductivity is[303] $9·5 \times 10^{-8}$ mhos.$cm.^{-2}$ for 0·01N solution and $4·0 \times 10^{-8}$ mhos.$cm.^{-2}$ for 0·001 N. solution. The coagulation effect of potassium sulphate on aqueous sols of silver chloride,[304] silver bromide,[304,305] silver iodide,[304,306] mercuric sulphide,[306] arsenious sulphide,[306,307] chromium hydroxide,[308] and ferric hydroxide[309] has been studied. The antagonistic action of mixtures of potassium sulphate and lanthanum nitrate in the precipitation of silver bromide or silver iodide sols has been considered in relation to the structure of the boundary layer between crystal and solution.[310] The effect of potassium sulphate on the conductivity, pH and viscosity of solutions of gelatin has been investigated.[311] The amount of adsorption of humic acid sols by graphite powder is increased in the presence of potassium sulphate.[312] The adsorption of potassium sulphate by pure soil colloids has been studied.[313] The adsorption of potassium from potassium sulphate solutions by hydrated manganese dioxide, MnO_2,H_2O, and by humic acid has been investigated in relation to the decomposition by these colloids of potassium sulphate in solution.[314] The behaviour of a charcoal-potassium sulphate mixture in the activated adsorption of different gases has been studied.[315] The adsorption isotherm for the system barium carbonate–potassium sulphate, in which barium carbonate was regarded as the adsorbent and potassium sulphate as the adsorbate, has been determined.[316] Static exchange between resins of RCl type and a mixture of potassium sulphate and potassium chloride has been investigated.[317] The effect of potassium sulphate on the critical micelle concentration of sodium dodecyl sulphate has been studied.[318] The addition of potassium sulphate to octanol–potassium tetradecanoate systems results in an initial marked increase in heptane solubility, followed by a decrease when the concentration of potassium sulphate is further increased.[319] The effect of potassium sulphate on the kinetics of adsorption from solution to the air–water interface has been investigated for solutions of hexadecyltrimethylammonium bromide and solutions of sodium dioctylsulphosuccinate.[320] The rate of solution of potassium sulphate in water is decreased by the presence of a protective colloid.[321] The effect of potassium sulphate on the stability of benzene-water and amyl alcohol-water emulsions has been measured.[322] The contraction of agar-agar gel on immersion in potassium sulphate solution has been investigated.[323]

Exchange experiments on aqueous solutions containing radioactive potassium sulphate, $K_2{}^{35}SO_4$, and inactive potassium persulphate, $K_2S_2O_8$, have indicated that there is no rapid exchange between sulphate and persulphate ions.[324] Isotopic exchange of sulphur trioxide with potassium sulphate has been observed;[325] when potassium sulphate and sulphur trioxide react to form potassium dipyrosulphate, substantial exchange occurs between excess sulphur trioxide and the sulphur originally in potassium sulphate.

The coefficient of diffusion of potassium sulphate vapour in the Bunsen flame is[326] 11·1 ± 10%.

Chemical Properties

Hydrogen begins to reduce potassium sulphate at 670° C.[327] Fluorine, free from hydrogen fluoride, does not react with solid potassium sulphate.[328] A solution of potassium sulphate when treated with fluorine liberates ozonized oxygen and the solution gives all the reactions of persulphates.[329]

Ammonia begins to reduce potassium sulphate at 800° C.[327] Liquid hydrogen fluoride probably reacts with potassium sulphate.[83] When excess of sulphur trioxide reacts with potassium sulphate at temperatures below 150°C., potassium pyrosulphate is first formed; the pyrosulphate then reacts rapidly with sulphur trioxide to form potassium dipyrosulphate, $K_2S_3O_{10}$. When a limited amount of sulphur trioxide reacts with potassium sulphate, the final products are potassium sulphate and potassium dipyrosulphate; these results apparently clarify previous seemingly contradictory results.[330]

After immersion for 24 hours in boiling 1N-potassium sulphate solution, aluminium is not appreciably attacked, copper is somewhat attacked, lead is noticeably attacked and zinc is appreciably attacked.[331] In the double decomposition reaction between calcium hydroxide and potassium sulphate, equilibrium can be shifted towards the formation of more potassium hydroxide by the presence of calcium aluminates which form insoluble calcium sulphate aluminates.[332] When calcium iodate is shaken continuously with a large excess of 0·5 molar potassium sulphate solution for several days, syngenite, $CaSO_4,K_2SO_4,H_2O$, is formed.[333] The precipitation of zinc hydroxide from solutions of potassium zincate by the addition of potassium sulphate has been studied.[334]

Potassium sulphate forms addition compounds with boron trifluoride and orthophosphoric acid. The compound K_2SO_4,BF_3 is formed by passing boron trifluoride over gently heated potassium sulphate;[335] it is a white crystalline substance which decomposes when heated and when dissolved in water. The crystalline compound $2K_2SO_4,H_3PO_4$ is precipitated when a solution of potassium sulphate in concentrated orthophosphoric acid is poured into alcohol,[336] and the crystalline compound K_2SO_4,H_3PO_4 is similarly formed from a hot solution of orthophosphoric acid saturated with potassium sulphate.[336]

Some double salts of potassium sulphate have been prepared: $3K_2SO_4,Na_2SO_4$ by heating a mixture of solid potassium and sodium sulphates;[337] $K_2SO_4,MSO_4,6H_2O$ by the reduction of potassium persulphate with metallic copper, magnesium, zinc, cadmium, manganese, iron, nickel or cobalt;[338] $K_2SO_4,2Al_2Br_6$ by dissolving potassium sulphate in molten aluminium bromide;[339] $2K_2SO_4,2TiOSO_4,5H_2O$ by the addition of solid potassium sulphate to a boiling solution containing titanium dioxide and sulphuric acid;[340] $3K_2SO_4,Bi_2(SO_4)_3$ by the addition of potassium sulphate solution to a concentrated solution of bismuth nitrate acidified with nitric acid.[155] Langbeinite could not be prepared from anhydrous potassium and magnesium sulphates.[109] The formation of complexes in aqueous solutions containing potassium sulphate and another salt has been detected. In solutions containing potassium and zinc sulphates, density and viscosity measurements have indicated the formation of a complex.[213] The complexes $K_2[Cu(SO_4)_2]$ and $K[Al(SO_4)_2]$ have been detected by refractometric measurements on aqueous solutions.[341] In aqueous solutions containing potassium sulphate and sulphuric acid, complex formation has been detected by the deviation from linearity between the acid function and the ionic strength of the solution.[342] Measurements of interfacial tension have shown the existence of two complex sulphates in solutions containing potassium sulphate and the sulphates of copper, cobalt, nickel, vanadium, zinc, magnesium or cadmium; and the existence of one complex sulphate in solutions of potassium sulphate and the sulphate of another alkali metal or silver.[343] The formation of anionic complexes between pyrophosphates and potassium sulphate has been studied.[344] Refractometric measurements have shown no complex formation in solutions of potassium sulphate with ammonium chloride.[341]

Electrolysis of potassium sulphate solution has shown the formation of persulphate and oxygen "in layer";[345] other sulphates were also studied and the most rapid and complete conversion of sulphate to persulphate was with potassium and ammonium sulphates.

The temperature at which thermal decomposition begins has been determined for various compositions of potassium sulphate-ammonium sulphate mixed crystals.[346] The reaction range of a mixture of potassium sulphate, potassium chloride and ammonium dichromate has been studied;[347] the plot of the explosion range of this mixture is not linear. The reaction of solid potassium sulphate with solid sodium sulphate and with solid magnesium sulphate monohydrate, $MgSO_4,H_2O$, has been investigated under a pressure of 6000 atmospheres.[348]

Diazomethane reacts with potassium sulphate in aqueous solution to give a 100% yield of potassium methyl sulphate, potassium hydroxide and nitrogen.[349] The combination of Novocaine with potassium sulphate has been studied.[350]

Applications

The industrial utilization of potassium sulphate has been reviewed.[351]

The effect of potassium sulphate fertiliser on sugar cane,[352] oat straw,[353] grass,[354] tobacco[355,356] and general crops[357] and of fertilisation with a mixed salt obtained from potassium sulphate and ammonium nitrate[358] has been investigated. The acidifying effect of potassium sulphate when applied to the soil has been studied.[359] The hygroscopicity of a phosphatic fertiliser has been reduced by the addition of potassium sulphate.[360] Potassium sulphate has been suggested as a constituent of a moulded organic fertiliser[361] and of phosphatic fertilisers.[362,363] The production of fertiliser from phosphate rock by fusion with potassium sulphate has been described.[364,365]

Potassium sulphate has been used to activate anhydrite binders.[366] The effect of potassium sulphate solution on the conversion of anhydrous gypsum to the dihydrate has been studied.[367] The effect of the addition of potassium sulphate to gypsum on the expansion[368,369] and strength[369,370] of gypsum and the effect of the addition of a mixture of potassium and aluminium sulphates on the hardness[371] of gypsum have been investigated.

Catalysts containing potassium sulphate have been used in dehydrogenation,[372] in the production of phthalic anhydride from tar oils[373] and in the conversion of durene to carboxylic acids.[374]

Potassium sulphate has been used in the preparation of easily soluble titanium compounds and of very pure titanium dioxide from ilmenite,[375] in the removal of fluorine compounds from sulphur dioxide in the manufacture of sulphuric acid,[376] in the preparation of glucose syrup,[377] in the water-proofing of gypsum products,[378] to improve the water-absorption characteristics of fibrous plaster-receiving surfaces,[379] in the preparation of potassium-containing nitrosulphato phosphates,[380] in concrete mixes,[381] and as a starting material for the manufacture of potassium sulphide.[382] The effect of potassium sulphate on the floatability of sulphate minerals,[383] on the fluidity of aqueous suspensions of china clay,[384] on the properties of tanned leather,[385] and on the formation of cream in GR-S latex[386] has been investigated. The potassium sulphate content of wines is increased by the addition of sulphuric acid at each withdrawal of the wine from storage casks.[387] The effect of slaking with potassium sulphate solution on the sedimentation of the resulting slaked line has been investigated.[388] Efflorescence of bricks and tiles is associated with potassium sulphate and other soluble sulphates.[389,390] A method of treating a mixture of solid potassium sulphate and sodium borate to decrease segregation has been described.[391] The products of the reaction of spodumene with potassium sulphate have been investigated.[392] The diffusion coefficient has been determined for solventless propellent powders containing potassium sulphate.[393] Potassium sulphate is formed at clinkering temperatures when potassium oxide and sulphur trioxide are present in cement mixtures.[394,395]

Analytical

The pharmacopoeial test for potassium sulphate as an impurity in aluminium acetate solutions has been discussed.[396] Potassium sulphate solution can be titrated against barium chloride or lead nitrate solution with a dropping mercury cathode.[397] Mixtures of potassium and magnesium sulphates can be analysed by heating to 1100°C., when only magnesium sulphate decomposes, and determining the resulting loss in weight.[398] In the determination of potassium in potassium sulphate by precipitation with calcium ferrocyanide, the precipitate is dissolved in dilute sulphuric acid and the resulting solution titrated with potassium permanganate.[399]

The use of potassium sulphate as a catalyst in the Kjeldahl method for nitrogen has been investigated.[400,401] A solution made by combining 10% potassium sulphate and 10% potassium fluoride solutions in a 6:1 ratio is an excellent alternative to the Zimmermann-Reinhardt reagent in the estimation of iron in ores.[402]

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POTASSIUM BISULPHATE

Preparation

Potassium bisulphate has been prepared by the fusion[1] of ammonium bisulphate and potassium sulphate in the presence of steam superheated to 200-400°C., and also by the evaporation[2] of a solution of potassium pyrosulphate over phosphorus pentoxide.

Physical Properties

X-Ray analysis of potassium bisulphate has shown[3] that the space lattice is Γ'_0, the lattice constants are:- $a = 8{\cdot}64 \pm 0{\cdot}02$ A., $b = 18{\cdot}86 \pm 0{\cdot}02$ A., $c = 9{\cdot}78 \pm 0{\cdot}01$ A., and the number of molecules in the unit cell is 16. For the absorption of β-rays by potassium bisulphate[4] the mass absorption coefficient is 16·9. The molecular magnetic susceptibility of potassium bisulphate is[5] $-49{\cdot}77 \times 10^{-4}$.

A study of the system potassium sulphate–sulphuric acid has indicated that potassium bisulphate is tetramorphous.[6] From measurements of the solubility of potassium bisulphate, the transition points between different forms of potassium bisulphate have been determined[7] as 164·2° and 184°C. in concentrated sulphuric acid from 135° to 200°C.

The density of potassium bisulphate at 16°C. is[3] 3·303 ± 0·001.

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The melting point of potassium bisulphate has been reported as[2] 216°C. and as[7] 211·7°C.

The entropy of fusion of potassium bisulphate is[8] approximately 23 g.-cal. mole^{-1} degree^{-1}. The heat capacities of aqueous potassium bisulphate solution at 25°C. have been determined[9] over a range of concentration and are given in Table XXIII.

TABLE XXIII. HEAT CAPACITY OF AQUEOUS POTASSIUM BISULPHATE SOLUTIONS AT 25°C.

Molality of Solution	c_p (g.-cal. gram^{-1} degree^{-1})
0·0498	0·99720
0·1017	0·99725
0·2483	0·99919
0·5547	1·00595
1·0151	1·01884
2·2442	1·06272

Mixed crystals of potassium bisulphate and potassium permanganate have been prepared.[10] The formation of solid solutions between potassium bisulphate and potassium borofluoride has been discussed[11] in relation to the lattice parameters. In the system potassium bisulphate-potassium pyrosulphate the eutectic temperature has been reported as[6] 201·2°C. and as[7] 203·5°C. and the corresponding composition as[6] 7·5 mole percent of the pyrosulphate and as[7] 5 mole percent of the pyrosulphate. The small fall in acidity shown by potassium bisulphate when treated with dry ethyl alcohol may be explained by regarding potassium bisulphate as composed of potassium sulphate and sulphuric acid with which ethyl alcohol forms a ternary system.[12] The density of 2·4310 molal aqueous potassium bisulphate solution is[9] 1·1922 at 25°C.

The conductivity of solid potassium bisulphate is[8] $2{\cdot}258 \times 10^{-10}$ ohm^{-1}cm.$^{-1}$ at 22·8°C., $1{\cdot}282 \times 10^{-9}$ ohm^{-1} cm.$^{-1}$ at 93·0°C., and $3{\cdot}682 \times 10^{-8}$ ohm^{-1} cm.$^{-1}$ at 168·0°C. The conductivity of molten potassium bisulphate is[8] 0·049 ohm^{-1} cm.$^{-1}$ at 211·8°C. and 0·141 ohm^{-1} cm.$^{-1}$ at 300·5°C. Small amounts of water adsorbed on powdered potassium bisulphate give rise to a sharp peak at about −30°C. in the temperature variation of dielectric constant and power factor of the solid.[13]

In potassium bisulphate solution, partial dissociation of the bisulphate ion, HSO_4^-, has been detected[14] by Raman effect measurements. By means of the Raman effect, the relative degrees of dissociation of potassium bisulphate have been determined[15] at four concentrations:- 13%, 1·00; 21%, 0·84; 28%, 0·68; 34%, 0·82. For potassium bisulphate solution, the plot of the number of undissociated potassium bisulphate molecules against concentration is in agreement with the equilibria of double ionisation.[16] The Raman spectrum of potassium bisulphate has been discussed[17] in relation to its electrolytic dissociation.

The use of potassium bisulphate as a catalyst in the dehydration of alcohols has been investigated. At 145°-150°C. and in the presence of potassium bisulphate as a catalyst, benzyl alcohol gives dibenzyl ether, 2-phenylethyl alcohol gives diphenylethyl ether and a mixture of alcohols gives the corresponding mixed ethers.[18] With the same catalyst, the lowest temperature at which olefins are formed from propyl alcohol is[19] 210°C. In such reactions potassium bisulphate is inferior to sodium bisulphate[19,20] and this smaller catalytic activity is related to its less hygroscopic nature.[21] Potassium bisulphate has been used as a catalyst also in the esterification of ethyl alcohol, propyl alcohol, and *iso*propyl alcohol with acetic acid, and in the esterification of ethyl alcohol with propionic acid.[22]

Potassium bisulphate, in quantities up to 0·1 mole fraction, does not reduce the rate of thermal decomposition of nitric acid sufficiently to prevent the eventual approach to equilibrium over storage periods of months at elevated ambient temperatures.[23] The depolymerization of paraldehyde at 25°C. in an aqueous solution of potassium bisulphate is a first-order reaction with respect to paraldehyde; the rate of reaction depends on the Hammett acidity function and on catalysis by undissociated species.[24] The presence of 0·2% of potassium bisulphate does not affect the action of ultrasonic vibrations on distilled water containing dissolved oxygen.[25] The effect of potassium bisulphate grit on the initiation of an explosion by friction and by impact in the solid secondary explosive P.E.T.N. has been studied;[26] potassium bisulphate has no effect on initiation by friction and the explosion efficiency (impact) is 2·5%. The effect of potassium bisulphate, used as a catalyst in the crystallization of gypsum from aqueous solution, on the crystalline form of the gypsum has been investigated.[27]

Both in the presence and in the absence of potassium bisulphate, no hydrogen-deuterium exchange was observed, at temperatures above 100°C., between tri-ethylmonosilane, tri-phenylmonosilane, or tri-ethoxymonosilane and deuterium oxide or deuterated ethyl alcohol.[28]

The thermal change of potassium bisulphate into the pyrosulphate, $2KHSO_4 \rightarrow K_2S_2O_7 + H_2O$, has been investigated;[7] the reaction is slow at 300°C., much more rapid at 350°C., and slightly faster still at 400°C.: the pressure from 140° to 250°C. is given by the equation:-

$$\log p_{mm} = (-3965{\cdot}60/T) + 9{\cdot}36683$$

Chemical Properties

A study of the action of fluorine on potassium bisulphate solution suggested that potassium persulphate was formed;[29] in later work[30,31] it was shown that a solution of potassium bisulphate treated with fluorine liberates ozonized oxygen and shows all the reactions of persulphate and that pure potassium persulphate could be isolated from the solution. The action of fluorine on solid potassium bisulphate also gave a product with all the reactions of persulphate.[32] Neither platinum nor a gold-platinum alloy containing 90% of gold is appreciably attached by potassium bisulphate below 400°C., but at 600°C. the alloy is attacked about twice as much as platinum.[33]

Potassium bisulphate begins to decompose slowly to the pyrosulphate at[2] 160° to 170°C. The thermal dehydration of potassium bisulphate does not go to completion, even under reduced pressure or in a current of sulphur trioxide.[6]

Crystallization of an aqueous solution of potassium bisulphate gave pure potassium sulphate; extraction of solid potassium bisulphate with ethyl alcohol removed sulphuric acid, leaving a residue of the normal sulphate.[34]

When equimolar mixtures of potassium bisulphate and dipotassium monohydrogen orthophosphate are heated, a highly exothermic proton-transfer reaction occurs at about 200° C. producing potassium sulphate and potassium dihydrogen orthophosphate.[35]

Treatment of leucite with aqueous potassium bisulphate solution yields alunite and a potassium micaceous mineral;[36,37] sanidine gives similar results.[37] Treatment of kaliophilite with aqueous potassium bisulphate solution yields newtonite and alunite.[37] Fusion with potassium bisulphate is a useful means of separating iron hydroxides and oxides from residues of heavy minerals thus facilitating the separation of unattacked minerals.[38]

Potassium bisulphate has been used in a rapid method of synthesis of organic reagents for qualitative analysis; e.g. trituration of 2-naphthol, sodium nitrite and potassium bisulphate for a few minutes gives a brown solid which

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can be used as 1-nitroso-2-naphtol for the detection of cobalt and zirconium.[39]

Applications

The applications of potassium bisulphate, with special reference to its agricultural uses, have been reviewed.[40] Potassium bisulphate has been used in the manufacture of potassium dichromate[41] and activated carbon,[42] in the solubilization of phosphatic fertilisers[43,44] in the activation of clays used as cracking catalysts,[45] in the dehydration of boleko oil,[46] as a catalyst in the emulsion polymerization of vinyl chloride,[47] as a flux,[48] and as a constituent of a reagent for the detection of sugar.[49]

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SECTION LVI

POTASSIUM CARBONATE

By W. H. LEE and M. F. C. LADD

Preparation

The concentration of potash ores such as sylvinite, langbeinite or halite, and their treatment by froth-flotation to produce a concentrate of the valuable ingredient of the ore, have been discussed.[1,2]

The electrolysis of a solution of potassium chloride (240g.) and potassium bicarbonate (140g. per litre) produces potassium carbonate in the cathode compartment; more potassium chloride is added to replace that consumed, and carbon dioxide is added to precipitate potassium bicarbonate.[3,4]

Potassium carbonate or potassium bicarbonate may be obtained from potassium carbamate, NH_2COOK, by hydrolysis. The carbamate may be prepared by the interaction of potassium chloride and ammonium carbamate in liquid ammonia.[5] Alternatively the treatment of potassium chloride in liquid ammonia with carbon dioxide, at a temperature greater than the decomposition temperature of the alkali carbamate, yields the bicarbonate directly.[6-9] Potassium chloride in liquid ammonia may also be treated with solid ammonium carbonate, and the product hydrolyzed as before.[10-12]

The passage of carbon dioxide through an aqueous solution of potassium chloride in the presence of an amine such as methylamine or dimethylamine,[13] or of a guanidine-formaldehyde mixture[14] yields potassium bicarbonate and the amine hydrochloride.

Potassium chloride is converted into potassium silicate, with liberation of hydrogen chloride, by heating with silica; the silicate is dissolved in water and treated with carbon dioxide to produce potassium carbonate and a precipitate of silica which is used again.[15]

Potassium chloride solution treated with syngenite (calcium potassium sulphate) in the presence of ammonia and carbon dioxide yields a mixture of potassium sulphate and calcium carbonate; further treatment with carbon dioxide under pressure converts the mixture to potassium bicarbonate and syngenite, the former being converted to potassium carbonate with lime.[16]

The aqueous extract of polyhalite, reduced by natural gas at 30°, gives a solution which contains potassium sulphide and at high concentrations is saturated with respect to potassium carbonate. On carbonation, 2000lbs. of polyhalite yield 320lbs. of potassium carbonate directly, and treatment of the residues with potassium chloride (sylvinite) yields additional potassium carbonate.[17]

The production of potassium carbonate from sylvinite solution has been described.[18,19] The mother liquor of the Solvay ammonia-soda process is treated with strontium sulphate, when strontium carbonate is formed: this when treated with sylvinite solution, and subsequently with carbon dioxide, reforms strontium sulphate, together with potassium carbonate and bicarbonate.

Potassium formate, made from potassium sulphate, an alkaline earth hydrate and carbon monoxide, gives potassium carbonate upon calcination;[20-22] in one process, this reaction is carried out at 200° and 15 atm.[23] A similar process employs calcium formate from which potassium formate is prepared by treatment with potassium sulphate.[24] The calcination may be effected in a rotary kiln.[25] Potassium formate may be converted into potassium bicarbonate by treatment with ammonium bicarbonate in aqueous alcohol; the potassium bicarbonate is sparingly soluble in this medium and is readily separated.[26] The 'formate' method has recently been reviewed.[27]

Potassium bicarbonate may be prepared by treating a solution of potassium acetate in ethanol with carbon dioxide and ammonia; the bicarbonate separates out,[28] and the alcoholic solution is treated with calcium hydroxide to produce calcium acetate which is subsequently converted to potassium acetate for re-use in the process.

A mixture of potassium sulphate, carbon and calcium oxide, heated to about 1000° in nitrogen, gives a product containing potassium cyanide; this is hydrolyzed with steam at 400°–500° to give potassium carbonate and ammonia:-[29,30]

$$2KCN + 4H_2O \rightarrow K_2CO_3 + CO + H_2 + 2NH_3$$

It was later suggested that the mixture of potassium sulphate, carbon and calcium oxide should be finely ground and briquetted before treatment with nitrogen.[31]

Potassium carbonate or bicarbonate is obtained by treating an aqueous suspension of potassium sulphate with barium carbonate in the presence of a stream of carbon dioxide. The barium sulphate is reconverted to barium carbonate by treatment with sodium carbonate,[32-34] or by reduction to barium sulphide before this treatment.[35] A mixture of granular potassium bicarbonate with finely ground potassium sulphate and barium sulphide is treated with boiling water. Hydrogen sulphide is eliminated on boiling, and the bicarbonate reacts with the potassium sulphide formed to yield a solution of potassium carbonate. Barium sulphide is regenerated from the precipitated barium sulphate.[36] In a modification of this process, the hydrogen sulphide is removed by an aqueous absorbent such as a solution of arsenious oxide.[37]

Potassium carbonate is obtained by treating a solution of potassium hydroxide with carbon dioxide in limited quantity, so that some of the hydroxide remains in the mother liquor to retain impurities in solution, potassium carbonate being precipitated.[38-40] The complete carbonation of potassium hydroxide solution has also been described.[41]

A solution of potassium dihydrogen phosphate or of dipotassium hydrogen phosphate is treated with ammonium carbonate or bicarbonate in the presence of free ammonia, preferably at about 0°. A precipitate of triammonium phosphate is obtained, and potassium carbonate is recovered from the filtrate. The ammonium phosphate may be treated with potassium chloride to give a potassium phosphate (KH_2PO_4 or K_2HPO_4) for re-use.[42,43] Alternatively, the potassium phosphate solution may be treated at about 0° with sodium carbonate or bicarbonate. In this procedure disodium hydrogen phosphate is precipitated: treatment of the filtrate with ammonia precipitates ammonium phosphate, and the filtrate then contains potassium carbonate.[44] A dilute solution of potassium phosphate (K_2HPO_4, 23•4% soln., for example) is saturated with ammonia in the presence of sufficient ammonium carbonate to convert all the potassium into potassium carbonate; triammonium phosphate is precipitated and the solution contains potassium carbonate.[45] Potassium carbonate is produced from potassium chloride in a two-stage process, comprising heating with calcium hydrogen phosphate in the presence of water at 700°–900° followed by passage of carbon dioxide through a suspension in water of the calcium potassium phosphate first formed.[46]

Potassium carbonate is made by adding magnesium oxide to a solution of a potassium salt, preferably the chloride, under a pressure of carbon dioxide equal to or higher than the critical pressure at which carbon dioxide is soluble in all proportions in water.[47] Similarly, potassium carbonate is produced by treating milk of calcined dolomite with carbon dioxide under pressure, filtering and then causing the solution to react with potassium chloride.[48]

The addition of magnesium oxide or hydroxide to a solution of a potassium salt saturated with carbon dioxide precipitates 'nascent' magnesium carbonate; treatment of this precipitate with a concentrated solution of a potassium salt gives a precipitate of Engel's salt, $KHMg(SO_3)_2,4H_2O$. Separation of this salt and its decomposition by heat in aqueous suspension forms insoluble magnesium carbonate and potassium bicarbonate solution.[49-58] The decomposition of Engel's salt has been considered in some detail;[59-62] one such process involves heating the salt with carbon in nitrogen to 950° to give potassium cyanide and magnesium oxide. Treatment with steam at 300°–500° gives the carbonate, the separated magnesium oxide reacting with potassium chloride to form a further quantity of Engel's salt.[63] The impure magnesium carbonate trihydrate obtained by decomposing Engel's salt is regenerated by conversion into an aqueous solution of magnesium bicarbonate, separating the solid residue, and recovering pure magnesium carbonate trihydrate from the solution for conversion into fresh Engel's salt.[64,65] The production thus becomes cyclic, and is known as the Engel–Precht process; this has recently been generally reviewed.[66]

Potassium carbonate may be obtained from mica by fusing with excess of potassium hydroxide, cooling, and extracting with water. The aqueous extract is treated with carbon dioxide; potassium carbonate may be extracted, or the crude mixture used directly, e.g. as a fertilizer.[67] Feldspar may be similarly treated, to yield potassium carbonate; in this case the mineral is fused with potassium carbonate (this being recovered),[68] or with a mixture of sodium and calcium carbonates.[69]

Finely-ground feldspar or orthoclase may be heated under pressure with sodium silicofluoride (Na_2SiF_6) solution; on cooling, K_2SiF_6 crystallizes out. A hot aqueous solution of this salt is treated with ammonia and carbon dioxide; $(NH_4)_2SiF_6$ and potassium carbonate are obtained.[70]

A mixture of nephelite, $(Na,K)AlSiO_4$, and limestone is heated to 1200° in a rotary kiln. The melt is ground, and lixiviated with sodium carbonate solution, to give an aluminate solution. Silica and phosphorus are removed by heating under pressure with calcium oxide; the filtrate is then treated with carbon dioxide at 80°–90°. Aluminium hydroxide is filtered off, and the sodium and potassium carbonates separated.[71]

Potassium carbonate may be extracted from leucite, $K_2O,Al_2O_3,4SiO_2$, by calcining it with limestone and fluorite at 930°;[72] the subsequent treatment is the same as for nephelite.[71]

Lava, and basic eruptives, such as wyomingite, contain the mineral leucite. The wyomingite is heated under pressure (at 200°) with sodium carbonate solution, and the solution evaporated and cooled; potassium sulphate remains in solution, but most of the silica is precipitated. The remainder of the silica is removed by treatment with magnesium carbonate; second-stage evaporation, and treatment with carbon dioxide, gives the double salt, Na_2CO_3,K_2CO_3, which is re-cycled, and a saturated solution of potassium carbonate.[73] The kinetics of the base-exchange reaction between wyomingite and sodium carbonate have been studied.[74]

The amount of potash in various plant by-product materials (up to 60% of the ash) justifies their consideration as a source of industrial potash. Methods of obtaining potash concentrates from the ash have been discussed.[75]

Molasses, and other by-products of the sugar industry, may be calcined in a limited supply of air; sulphates are reduced to sulphides, and treatment of an aqueous extract with carbon dioxide yields potassium carbonate.[76,77] Prior addition of potassium sulphate improves the yield of potassium carbonate.[80] Processes for obtaining potash, sodium cyanide and ammonium sulphate from molasses distillery residues have been reviewed.[78] Incineration of molasses at a low temperature yields a crude potash fertilizer.[79] In an alternative method, the molasses is allowed to ferment after the pH of the diluted solution has been adjusted to 4·0. Calcium sulphate is separated, and concentration and carbonization at 830° produces decolorizing carbon and potassium carbonate; the carbon dioxide formed in the fermentation may be recovered.[81]

Purification.

A number of methods have been suggested for the elimination of sodium carbonate from potassium carbonate. These include passing the solution through a potassium zeolite;[82] conversion to, and separation of, the bicarbonates;[83] evaporation of the concentrated mixed aqueous solution and cooling to −15°;[84-86] and fractional crystallization.[87]

Passing potassium carbonate solution through an ion-exchange resin, such as Amberlite I R 120 in the hydrogen form, removes potassium hydroxide from the solution; this has been found desirable in the preparation of labelled potassium carbonate by passing $^{14}CO_2$ into potassium hydroxide solution.[88]

Alkali metal chlorides are separated from solutions of crude potassium carbonate by saturation with ammonia gas; two layers are formed, having 27g. KCl + 17g. K_2CO_3 per litre in the upper layer, and 740g. K_2CO_3 + 4g. KCl per litre in the lower layer.[89,90] Alternatively, electrolysis of the solution between silver electrodes, with an anode current density of 20–30 microamperes per square cm., reduces the chloride content practically to zero, the optimum concentration of solution being 1·5 mol. K_2CO_3/l.[91]

Dissolved silica may be removed by crystallization, on cooling from 100° to 25°; the remaining silica (about 20% of the original silica content) may be adsorbed at 27° on hydromagnesite ($3MgCO_3,Mg(OH)_2,3H_2O$).[92]

Specification for Purity.

For the detection of bicarbonate in potassium carbonate, a 20% solution is prepared: then 30 c.c. of barium nitrate solution and 3 drops of phenolphthalein are added. No red colour should develop after mixing and allowing to stand in a well-stoppered bottle for 3 minutes. The addition of 0·1 c.c. of 0·1N. caustic soda solution should impart a permanent red colour to the solution. The test is sensitive to 0·1% of bicarbonate.[93]

A specification for 'A.R.' potassium carbonate has been drawn up, as shown in Table I.[94]

TABLE I. - SPECIFICATION FOR 'A.R.' POTASSIUM CARBONATE

Impurity	Limit %
Insoluble matter	Not greater than 0·02
Loss on ignition	Not greater than 1·0
Cl' and ClO_3'	About 0·003 as Cl'
Sulphate	Not greater than 0·004
Nitrogen	Not greater than 0·001
Phosphate	Not greater than 0·005
Silica	Not greater than 0·005
NH_4OH ppt.	Not greater than 0·005
Ca and Mg ppt.	Not greater than 0·015
As	Not greater than 0·0003
Na	About 0·02
Heavy metals, Pb	Not greater than 0·0005
Heavy metals, Fe	Not greater than 0·001

Potassium carbonate of regular granularity may be obtained by cooling or evaporating its solution in order to precipitate the salt as fine crystals; these are dried, fused in a rotary furnace, and subjected to an air blast as the fused mass is poured from the furnace.[95] Alternatively, a solution of 28 parts of potassium hydroxide in 28 parts of water with 100 parts of potassium carbonate is led into a rotating, inclined, thermally-lagged iron tube, coated with nickel or silver. Carbon dioxide is led in at 15°–65°, and after 20–25 minutes potassium carbonate is obtained in granular form in 98% yield.[96]

It has been suggested that the tendency for potassium carbonate to form hard lumps during storage may be overcome by admixture of 1–2% of potassium bicarbonate, though such potassium carbonate may be termed only 'commercial'.[97]

Physical Properties

Crystals of potassium bicarbonate are monoclinic prismatic, the unit cell containing four molecules, and having the dimensions shown in Table II.

TABLE II. - MEASURED LATTICE PARAMETERS OF POTASSIUM BICARBONATE, IN A.

a	*b*	*c*	*β*	Ref.
15·01	5·69	3·68	104°30′	98,99
15·04 ± 0·04	5·51 ± 0·02	3·68 ± 0·01	104°30′	101
15·11	5·67	3·71	103°45′	102
15·176 ± 0·003	5·630 ± 0·002	3·708 ± 0·002	104°31′	101a

The space group is $C_{2h}^5 - P2_1/a$;[98-101] the CO_3 group has C–O distances 1·28, 1·32 and 1·33A. and is planar.[102] The two O atoms with the longer C–O distances are H-bonded in pairs to another CO_3 group with O–H. . .O distance 2·61A., so that a complex anion $(H_2C_2O_6)^{--}$ is formed.[102] A recent goniometric examination gives the following values for interfacial angles:-

$100:20\bar{1}$, 76°17′
$100:40\bar{1}$, 53°8′
$20\bar{1}:40\bar{1}$, 23°5′

in good agreement with those calculated from previous *X*-ray work.[103]

The following interfacial angles have also been reported:-[104]

001:100, 76°35′
100:101, 53°25′
001:101, 23°10′

Two species of crystalline 'stone' have been found in the trunks of standing, partly-burned trees: fairchildite, $K_2CO_3,CaCO_3$, hexagonal, $\epsilon = 1{\cdot}48$, $\omega = 1{\cdot}530$, and buetschliite, $3K_2CO_3,2CaCO_3,6H_2O$, probably also hexagonal, with $\epsilon = 1{\cdot}455$ and $\omega = 1{\cdot}595$. The corresponding compounds have been synthesized.[105]

The infrared spectra of potassium bicarbonate and potassium carbonate have been investigated. Absorption bands appear at 6μ, 7·3μ, 10μ and 12μ, for the bicarbonate; and at 6·9μ and 11·4μ for the carbonate.[106]

The hydrogen bond in potassium bicarbonate has been studied by investigating the Raman spectra of single crystals. The distortion of the vibration pattern of the ion as compared with the energy levels of such compounds as calcium carbonate indicates the existence of a perturbation, such as might arise from hydrogen bonding between O atoms in adjacent ions. Data on the spectra are tabulated.[107] Distinctive chemiluminescence is observed at a potassium carbonate surface on which the combination of hydrogen atoms, and the H–OH reaction, are occurring.[108]

The density of potassium carbonate, at 25°, is 2·426. The coefficient of thermal expansion, α, has the following values:-[109]

Temperature range:	19° to −78°	−78° to −183°	−183° to −273°
$10^5\alpha$	13	9	4

The dissociation pressure of potassium carbonate, according to the reaction:-

$$K_2CO_3 \rightleftharpoons K_2O + CO_2$$

has been measured at various temperatures; the results are given in Table III.

TABLE III. - DISSOCIATION PRESSURE OF POTASSIUM CARBONATE, IN MM. OF MERCURY

t°	p mm.	Ref.
900	0	111
950	1·2	111
970	1·68	110
1000	2·1	111
1100	7·4	111
1200	10·3	111
1300	15·1	111
1400	35·6	111

The melting point of potassium carbonate is 891°.[109,112] The decomposition velocity of potassium bicarbonate follows the Arrhenius equation, with activation energy 24·45 kg.-cal./mole.[113] The enthalpy change of the dissociation, $\Delta H_{291}^{\circ} = 94{\cdot}26$ kg.-cal./mole.[114]

Thermodynamic data for the decomposition of potassium bicarbonate:-

$$2KHCO_3 \rightarrow K_2CO_3 + CO_2 + H_2O(g)$$

are as follows:-

$$\Delta H_{298} = 32{\cdot}44 \text{ kg.-cal./mole}$$
$$\Delta G_{298} = 10{\cdot}76 \text{ kg.-cal./mole}$$
$$\Delta S_{298} = 73 \text{ e.u.}$$

For the formation of potassium bicarbonate, according to the theoretical process:-

$$K + \tfrac{1}{2}H_2 + C(\beta\text{-graphite}) + \tfrac{3}{2}O_2 = KHCO_3,$$
$$\Delta Gf_{298} = -209{\cdot}5 \text{ kg.-cal./mole}$$
$$S_{298} = 26 \text{ e.u.}$$
$$\Delta Hf_{298} = -233{\cdot}3 \text{ kg.-cal./mole}^{114}$$

A more recent value for ΔHf_{298} is −229·3 kg.-cal./mole.[114a] The following values are given[114a,b] for the heat of formation of potassium carbonate:-

ΔGf_{298} for: K_2CO_3 −251·5 kg.-cal./mole $S_{298} = 36{\cdot}1$ e.u.
ΔHf_{298} for: K_2CO_3 −273·9 kg.-cal./mole $\Delta Hf_{298} = -272{\cdot}1$
$K_2CO_3\tfrac{1}{2}H_2O$ −210·4 kg.-cal./mole
$K_2CO_3\tfrac{3}{2}H_2O$ −283·4 kg.-cal./mole

Potassium carbonate shows two second-order transitions, at 410° and 465°; by comparison, sodium carbonate shows a second-order transition at 360°, and a first-order transition at 480°. The second-order transitions of potassium carbonate are indicated by anomalies in specific heat and thermal expansion data.[115]

The rate of thermal decomposition of potassium bicarbonate has been studied at 140°–200°, using a thermobalance. The results may be interpreted by the four-stage decomposition:-

$$KHCO_3 \rightarrow 5KHCO_3K_2CO_3 \rightarrow 2KHCO_3K_2CO_3 \rightarrow KHCO_3K_2CO_3 \rightarrow K_2CO_3.$$[116]

It appears doubtful, however, whether these species correspond to definite chemical compounds.

The rate of decomposition of potassium carbonate in a stream of nitrogen has been studied in the presence or absence of water vapour and of solid promoters such as silica and alumina. Within the temperature range 200°–700°, water vapour increases the rate and the promoters are more effective in the presence of water vapour. A maximum rate of decomposition is observed at 500°-600°.[117]

The dielectric constant of potassium carbonate at 18° and 166·6 kcs./sec. is 4·96.[118] The mean dielectric constant ($\bar{\epsilon}$) for bulk crystals of potassium bicarbonate has been calculated from Böttcher's equation[119] applied to data for the powder; the value obtained, at 10 kcs./sec. was 4·31 ± 0·03. From the equation $\alpha_m = \frac{3V(\bar{\epsilon} - 1)}{(\bar{\epsilon} + 2)}$ (where V is the molecular volume in A^3., and α_m the mean molecular polarizability) α_m for potassium bicarbonate was found to be 119·8, V being given by X-ray measurements as 76·0 c.c.[119a] Taking Roberts's values[119b] for the polarizabilities of the sodium and potassium ions, the ionic polarizability of the bicarbonate ion was calculated to be 87·5 in sodium bicarbonate, and 77·5 in potassium bicarbonate. It is concluded that the protons in these bicarbonates do not possess the freedom postulated for protons in the hydrogen-bonded solids potassium dihydrogen phosphate and ice.[119a]

Considering the physical properties of aqueous solutions, the refractive index and molar refraction have been measured for a number of solutions of potassium carbonate, at 25° and at sodium D wave-length (5893A.); the results are listed in Table IV.

TABLE IV. - REFRACTIVE INDEX, AND MOLAR REFRACTION, OF AQUEOUS POTASSIUM CARBONATE, AT 25°.[120]

Concn., g.-equiv. per kg. water	d_4^{25}	n_D^{25}	$[R_D]$
0	0·99707	1·33254	(8·349)
0·9684	1·05309	1·34314	8·360
1·9847	1·10709	1·35286	8·363
3·1046	1·16191	1·36233	8·370
4·0837	1·20614	1·36967	8·377

The temperature at which the coefficient of thermal expansion of an aqueous solution becomes equal to that of water, called by Mendeleev the 'characteristic temperature', t_c, is for potassium carbonate approximately 50°.[121]

The viscosity and density of aqueous solutions of potassium carbonate, and of mixed aqueous solutions of potassium carbonate and potassium hydroxide, have been measured at three temperatures: 20°, 30° and 40°. Table V records the results at 20° for pure potassium carbonate solution, and for the intermediate potassium hydroxide concentration studied (46·3 wt.-%); other potassium hydroxide concentrations considered were 24·1% and 72·3%.[122]

The solubilities of potassium carbonate and potassium bicarbonate in water at various temperatures, and the densities of the solutions, are listed in Table VI and Table VII.[123]

At 18°, 82·5g. of potassium carbonate dissolves in 100 c.c. of saturated

TABLE V. - VISCOSITY AND DENSITY OF AQUEOUS SOLUTIONS OF POTASSIUM CARBONATE, AND OF POTASSIUM CARBONATE-POTASSIUM HYDROXIDE, AT 20°

g.-equiv./l.	$d_4^{20°}$	η, centipoise
Potassium Carbonate		
0•9479	1•0526	1•1459
1•820	1•1003	1•3051
2•780	1•1514	1•5184
3•616	1•1945	1•7638
4•421	1•2349	2•0372
5•268	1•2764	2•3677
6•097	1•3159	2•7925
7•112	1•3631	3•4422
Potassium Carbonate–Potassium Hydroxide (46•3%)		
0•9178	1•0474	1•1227
1•781	1•0967	1•2538
2•810	1•1404	1•4479
3•677	1•1804	1•6434
4•695	1•2257	1•9237
5•480	1•2589	2•1582
6•267	1•2918	2•4665
7•332	1•3341	2•9619

TABLE VI. - SOLUBILITY AND DENSITY OF SATURATED SOLUTIONS OF POTASSIUM CARBONATE

$t°$	$d_{\text{soln.}}$	g. K_2CO_3 per 100g. sat. soln.
-11	1•533	50•45
-5	1•545	50•93
0	1•546	51•35
5	1•548	51•60
10	1•549	51•90
30	1•557	53•60
50	1•570	55•73
70	1•590	58•13

TABLE VII.- SOLUBILITY AND DENSITY OF SATURATED SOLUTIONS OF POTASSIUM BICARBONATE UNDER 1 ATMOSPHERE PRESSURE OF CARBON DIOXIDE

$t°$	$d_{\text{soln.}}$	g. $KHCO_3$ per 100g. sat. soln.
0	1•133	18•41
10	1•154	21•53
20•5	1•177	25•23
30	1•200	28•52
40	1•220	32•24
50	1•244	36•04
60	1•271	39•65
70	1•301	43•37

sodium carbonate solution.[124] The molality of a saturated solution of potassium bicarbonate in water at 25° is 3•60; that of the hydrate $K_2CO_3,\frac{3}{2}H_2O$ at 25° is 8•22.[114]

Solubility isotherms in the systems potassium carbonate–potassium sulphate–water and potassium bicarbonate–potassium sulphate–water at 50° have been determined.[125]

Potassium carbonate is insoluble in liquid ammonia at 25°; in water, at this temperature, 1·458 moles dissolve in 10 moles of solvent.[126]

Potassium carbonate is considerably more soluble in methyl alcohol than in ethyl alcohol, acetone or ether; the significance of these results, from the point of view of Soxhlet extraction, has been considered.[127]

The surface tension of a 2·65 molar aqueous solution of potassium carbonate is 82·2 dynes/cm. at 15°.[128]

The interfacial tension between water and mercury at 20°, 375 dynes/cm., is unaffected by addition of potassium bicarbonate; the interfacial tension between molar potassium carbonate solution and mercury is 381·6 dynes/cm.[129]

The surface tension of aqueous solutions of potassium carbonate has been measured at 20° with the results recorded in Table VIII.[130]

TABLE VIII. - DENSITIES AND SURFACE TENSIONS OF AQUEOUS POTASSIUM CARBONATE SOLUTIONS AT 20°

Wt.-% water	Mols. water/l. soln.	d_4^{20}	γ, dynes/cm.
50	42·8	1·543	103·8
55	45·1	1·478	96·6
60	47·2	1·416	91·4
65	49·0	1·358	87·3
70	50·5	1·299	83·8
80	52·9	1·191	78·6
90	54·6	1·092	75·1
100	55·4	0·9982	72·75

Density, molarity and apparent molar volume of concentrated aqueous solutions of potassium carbonate have been measured; the curve relating molar volume to the square root of the concentration is linear only as far as 2·2N. Values are listed in Table IX.[131]

TABLE IX. - DENSITY AND APPARENT MOLAR VOLUME AT 25° OF CONCENTRATED AQUEOUS SOLUTIONS OF POTASSIUM CARBONATE

(Molarity)$^{1/2}$	d_4^{25}	Apparent molar vol. (c.c.)
0·9777	1·20614	10·52
1·390	1·16192	12·19
1·723	1·10710	13·64
1·960	1·05310	14·72

The volume of water of hydration, per mole of potassium carbonate, is 390 c.c. at 30°.[132]

The boiling-point:pressure relationship for potassium carbonate solutions in water is shown in Fig. 1, which is typical over a wide range of concentrations.[133]

Potassium carbonate salts out ethyl alcohol from its concentrated aqueous solution; the composition of the two liquid layers has been determined at 25°, 50° and 75°. In the three-phase systems, the total vapour pressure, and the partial pressure of ethanol, show minima at medium concentrations of both potassium carbonate and ethyl alcohol. For example, at 50° the total vapour pressure and the partial vapour pressure of ethanol are minimal, at 191·5 and 115·4 mm.Hg respectively, when the concentration of ethanol is 15·75% in the lower layer and 31·17% in the upper layer.[134]

Isothermal dehydration curves for potassium carbonate have been drawn;

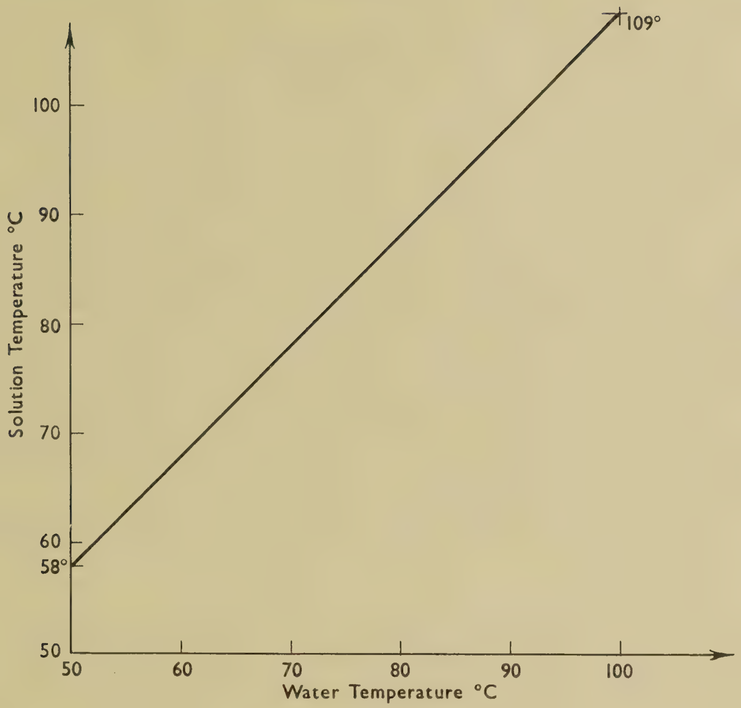

FIG. 1. BOILING POINT:PRESSURE RELATIONSHIP FOR POTASSIUM CARBONATE SOLUTIONS AS COMPARED WITH THAT FOR WATER CONCENTRATION = 85·90 g.K_2CO_3/100g.H_2O

the heat of hydration, to $K_2CO_3,2H_2O$, has been calculated as 10·1 kg.-cal./mole.[135]

Kinetic studies have been made of the absorption of gases by aqueous solutions of potassium carbonate.

The absorption of carbon dioxide by alkali metal hydroxide and carbonate solutions has been studied. The rate of absorption of carbon dioxide per sq. cm. in hydroxide solutions is $(Dk[OH^-])^{1/2}[CO_2]$, where D is the diffusivity of free carbon dioxide, k is the reaction rate constant for the process: $CO_2 + OH^- \rightarrow HCO_3^-$, $[OH^-]$ is the concentration of hydroxyl ions in solution, and $[CO_2]$ is the concentration of carbon dioxide at the interface.[136] For potassium carbonate solutions at 30°C. and under a pressure of carbon dioxide of 1 atm., the initial rate of absorption of the gas may be expressed by:-

$$\frac{1}{A}dM/d\theta = k(C_s - C_i)^b/Z,$$

where M is millimoles of carbon dioxide absorbed in time θ hours, A is the surface area in cm.^{2}, C_s is the concentration of the carbonate solution in g.-equiv. per litre, C_i the interfacial concentration of carbon dioxide, and Z the viscosity in centipoises. This is a general equation applying also to absorption by alkali hydroxide solutions. For potassium carbonate, the specific values of k and b are 0·45 and 0·443 respectively. It is concluded that, for absorption of carbon dioxide under batch conditions, the rate is largely governed by the rate of diffusion of the gas through the liquid.[137] For the equilibrium:-

$$K_2CO_3 + H_2O + CO_2 \rightleftharpoons 2KHCO_3,$$

the equilibrium constant, defined by:-

$$K = \frac{[KHCO_3]^2}{[K_2CO_3].p_{CO_2}},$$

varies with temperature as follows:-

$t =$	30°	40°	50°	60°	70°	80°	97°
$K =$	0.239	0.182	0.132	0.096	0.068	0.045	0.023

The rate of absorption of carbon dioxide by potassium carbonate solutions is proportional to the partial pressure of carbon dioxide, p_{CO_2}: the rate is almost independent of temperature for 2N. carbonate solutions, but increases with increasing concentration and with stirring.[138] Equilibrium at the interface is attained in less than five milliseconds; solute gas molecules diffuse from the interface into the liquid interior as chemical reaction proceeds.[139] The rate of absorption of carbon dioxide is greater for potassium hydroxide solution than for potassium carbonate solution, and very much greater for potassium bicarbonate solution, under varying conditions of temperature, pressure, concentration and stirring.[140,140a]

On the plant scale, the effect of variation of flow rates of liquid and gas, and of the packing of absorption columns, upon the rate of absorption of carbon dioxide by mixed solutions of potassium hydroxide and potassium carbonate has been studied.[141]

The rate of absorption of bubbles of carbon dioxide by potassium carbonate solution at various temperatures depends upon the carbonate:bicarbonate ratio; the rate is greatest at high temperatures in carbonate-rich solutions and greatest at low temperatures in bicarbonate-rich solutions. For an unbroken surface the rate is proportional to the pressure of carbon dioxide at low pressures of the gas; at higher pressures it is more dependent upon the concentration of the solution, and in this respect resembles the absorption of hydrogen sulphide.[142]

The absorption of hydrogen sulphide at pressures within the range 0.02–0.7 atm. is very dependent upon the concentration of the absorbent in solution but not upon the partial pressure of the gas; at low partial pressures, however, the concentration of absorbent does not affect the rate which is then markedly dependent upon partial pressure.[143] For dilute solutions of potassium carbonate the absorption process is:-

$$K_2CO_3 + H_2S \rightarrow KHCO_3 + KHS.$$

For a 2N. solution of potassium carbonate the equilibrium constant K_1 is:-

$$K_1 = \frac{[KHCO_3][KHS]}{[K_2CO_3].p_{H_2S}},$$

where p_{H_2S} is the partial pressure in mm.Hg. K_1 has the value 0.074 mole/litre mm. at 25°C. The relationship between p_{H_2S} and the concentration of hydrogen sulphide present in a 2N. solution of potassium carbonate at equilibrium c may be expressed by:-

$$p_{H_2S} = 0.714(t + 43).c^{2.88}$$

which holds within the temperature range 25°–60°. K_1 is related to the temperature[144] by the equation:-

$$\log K_1 = (2800/4.576T) - 3.2.$$

For simultaneous absorption of carbon dioxide and hydrogen sulphide, we have the further processes:-

$$K_2CO_3 + CO_2 + H_2O \rightleftharpoons 2KHCO_3 \; . \; . \; . \; . \; . \; . \; . \; (1)$$
$$KHS + CO_2 + H_2O \rightleftharpoons KHCO_3 + H_2S \; . \; . \; . \; . \; . \; (2)$$

Equilibrium in this system is determined by the constant K_3 representing the ratio of K_1 in the previous system to K_2 for the system: $CO_2 - K_2CO_3 - KHCO_3 - H_2O$; K_3 is of the order unity, and the equation (2) above is readily reversible. The ratio $[H_2S]/[CO_2]$ absorbed does not vary significantly with the concentration of the solution. K_3 increases with decrease of temperature, and lower temperatures favour the absorption of a higher proportion of carbon dioxide.[144]

The effect of electro-osmosis on paper electrophoresis of 0·025M. potassium carbonate solution has been studied; 0·060g. of electrolyte were transported, and the boundary moved 2·61cm. in one hour.[145] The electrocapillary maximum for 0·1N. potassium carbonate solution at 25°C. is 0·473V. referred to the normal calomel electrode. At this value, the potential (E) between mercury and the solution changes with the chemical potential (μ) of the electrolyte according to: $dE/d\mu = 0{\cdot}132$, and the capacity of the electrical double layer on mercury is 22·0μF. per sq.cm.[146] The surface charge density (q) on mercury in 0·1N. potassium carbonate at 25° has been measured; the results at varying interfacial potentials (E) measured relative to the normal calomel electrode are listed in Table X.[147]

TABLE X. - SURFACE CHARGE DENSITY IN MICROCOULOMBS PER CM.^{2}Hg IN 0·1N. POTASSIUM CARBONATE AT 25°

$-E$	q	$-E$	q	$-E$	q
0·12	13·19	0·68	−4·21	1·40	−16·45
0·20	9·02	0·80	−6·49	1·50	−18·19
0·28	5·51	0·90	−8·26	1·60	−20·01
0·36	2·87	1·00	−9·94	1·70	−21·95
0·44	0·762	1·10	−11·57	1·80	−24·03
0·52	−0·997	1·20	−13·16		
0·60	−2·623	1·30	−14·79		

The zeta-potential of potassium carbonate solutions at a cellulose interface has been derived from measurements of streaming potentials by the relationship: $\zeta = 4\pi H\eta\kappa_S/PD$, where ζ is the zeta-potential, and H the streaming potential, both in millivolts, η is the coefficient of viscosity, κ_S is the surface specific conductivity in mhos, D is the dielectric constant and P the pressure in cm.Hg under which streaming occurs. The results are recorded in Table XI.[148]

TABLE XI. - STREAMING POTENTIALS AND ZETA-POTENTIALS, AT A CELLULOSE INTERFACE IN POTASSIUM CARBONATE SOLUTIONS

10^3normality	p cm. Hg, range	mean H/P	$10^6(\kappa_S/\kappa)$*	$10^2\eta$	ζmV.
0	65–83	−4·405	14·23	0·945	−11·5
0·1	72–85	−3·472	32·43	0·894	−16·44
0·2	65–85	−1·857	66·50	0·950	−17·58
0·4	67–87	−1·206	91·10	0·955	−17·19
0·8	75–85	−0·6969	133·6	0·945	−15·87

* κ is the bulk specific conductivity of the solution

An equation relating electrical conductivity and vapour pressure of a solution is: $K\log p_0/p + rC = nF$, where K is a constant at a given temperature, p_0 is the vapour pressure of water and p that of the solution at this temperature,

C the specific conductivity of the solution and n the concentration in moles per 100g. of water. At 100°, K has the value 3926. For potassium carbonate solutions, taking the vapour pressure measurements of Tammann,[149] and electrical conductivities at 100° determined by Dahlblom,[150] the following values of the constants r and F were deduced: $r = 311$, $F = 149$.

Aqueous vapour pressures have been measured for the saturated solution of potassium carbonate dihydrate, $K_2CO_3,2H_2O$ (1), and for the equilibrium:-

$$K_2CO_3,2H_2O\ (\text{solid}) \rightleftharpoons K_2CO_3\ (\text{solid}) + 2H_2O\ (\text{gas})\ (2).$$

The results, in mm. of mercury at various temperatures, are recorded below:-[151]

Temp., t°	15	20	25	30	35	40
p, mm.(1)	5·9	7·3	10·0	13·1	16·25	–
p, mm.(2)	–	–	0·59	0·85	1·24	1·78

Apparent and partial molal volumes of potassium carbonate, in solutions of sodium chloride, have been determined from density measurements at various concentrations of both salts, at 25°. The results are shown in Table XII.[151]

TABLE XII. - APPARENT AND PARTIAL MOLAL VOLUMES OF POTASSIUM CARBONATE IN SODIUM CHLORIDE SOLUTIONS AT 25°

Molarity NaCl	K_2CO_3	$\sqrt{\text{Volume ionic strength}}$, μ_v	Density	$\bar{V}_3$	ϕ_3
0·04065	0	0·20162	0·99876	15·07	15·07
0·04061	0·05389	0·44976	1·00531	18·00	16·69
0·04057	0·11756	0·62278	1·01292	19·76	17·82
0·04048	0·21636	0·83040	1·02448	21·80	19·18
0·04038	0·32289	1·00451	1·03686	23·51	20·32
0·1629	0	0·40361	1·00378	18·01	18·01
0·1627	0·05184	0·56411	1·00995	20·61	19·18
0·1625	0·11577	0·71401	1·01743	22·41	20·27
0·1622	0·20953	0·88926	1·02826	24·41	21·54
0·1617	0·32643	1·06817	1·04141	26·41	22·85
0·3599	0	0·59992	1·01176	20·74	20·74
0·3595	0·05475	0·72371	1·01812	23·35	21·73
0·3590	0·11375	0·83681	1·02488	24·97	22·64
0·3581	0·21704	1·00460	1·03651	27·20	23·98
0·3569	0·32506	1·15416	1·04838	29·10	25·18
0·6430	0	0·80187	1·02305	22·26	22·26
0·6422	0·05399	0·89676	1·02924	24·39	22·94
0·6412	0·11773	0·99719	1·03647	25·80	23·64
0·6397	0·21094	1·12806	1·04694	27·46	24·61
0·6374	0·33479	1·28132	1·06047	29·29	25·71
0·9922	0	0·99609	1·03693	25·99	25·89
0·9908	0·05304	1·07234	1·04279	28·76	26·69
0·9890	0·11733	1·15801	1·04982	30·66	27·58
0·9860	0·21555	1·27775	1·06033	32·98	28·82
0·9825	0·32583	1·39999	1·07182	35·19	30·10

Note: The apparent molal volume, $\phi_3$ml., is obtained from the equation:-

$$\phi_3 = \frac{V - (n_1\bar{V}_1^0 + n_2\phi_2)}{n_3},$$

where V is the total volume of solution, n_1 the number of moles of solvent, n_2

and n_3 the number of moles of sodium chloride and potassium carbonate, respectively, and ϕ_2 is the apparent molal volume of sodium chloride in aqueous solution of composition n_1n_2. The partial molal volume, $\bar{V}_3$, is given by:-

$$\bar{V}_3 = \left(\frac{\delta V}{\delta n_3}\right)_{n_1,n_2}.$$

The electromotive force of cells of the type shown below, involving potassium carbonate solution in methanol or ethanol, has been measured with the results recorded in Table XIII.[152]

TABLE XIII. - E.M.F. AT 50°C. OF THE CELL $Hg/HgCl, KCl(N.)/K_2CO_3AQ.(c_1)/K_2CO_3(c_2 \text{ IN } ROH)/KCl(N.), HgCl/Hg$

Solvent	c_1*	c_2*	c_1/c_2	E(mV.)
MeOH	9·463	1·020	9·27	5·1
MeOH	6·494	2·451	2·65	3·9
EtOH	10·472	0·0078	1348	21·8
EtOH	8·016	0·0247	323·8	19·5
EtOH	4·595	0·552	8·3	4·3
EtOH	3·177	1·444	2·2	3·9
EtOH	3·175	1·444	2·2	3·2

*c_1 and c_2 are in moles/litre

In an investigation of the first ionization constant of carbonic acid, the electrical conductivity of aqueous solutions of potassium bicarbonate was measured at 25°; the conductances are recorded in Table XIV.[152a]

TABLE XIV. - ELECTRICAL CONDUCTIVITY OF AQUEOUS SOLUTIONS OF POTASSIUM BICARBONATE AT 25°

10^3c(g.-equiv./l.)	$\Lambda_{obs.}$	$\Lambda_{calc.}$
0	-	118·00
0·8773	115·55	115·51
1·8312	114·48	114·43
4·4866	112·50	112·54
10·571	109·83	109·87
19·639	107·27	107·30

$\Lambda_{calc.}$ was obtained from the Onsager equation in the form:-

$$\frac{\Lambda + 59\cdot79c^{1/2}}{1 - 0\cdot2274c^{1/2}} = 118\cdot00 + 76\cdot0c$$

The electrical conductivity of solutions of potassium carbonate in varying concentrations of potassium hydroxide solution has been measured at 25°, 50° and 97°C.[153] The results at 25° are recorded in Table XV.

Viscosity in the system $KOH-K_2CO_3-H_2O$ has been measured at 25° and 50° for two particular concentrations of potassium hydroxide: the results are given in Table XVI.[153]

The electrical conductivities of solutions of potassium carbonate and potassium bicarbonate in 15°Brix (15·8876g. per 100ml.) and Normal (26·026g. per 100ml.) sucrose solutions have been measured with the results shown in Table XVII.[154]

From the relationship:-

$$\left\{1 + \frac{b(c_0 - c_1)}{c_0}\right\}^{-1} = \text{constant}, A,$$

TABLE XV. - ELECTRICAL CONDUCTIVITY IN THE SYSTEM $KOH–K_2CO_3–H_2O$ AT 25°

Wt.-%KOH	Wt.-%K_2CO_3	$10^5\kappa$ mhos
18·86	-	0·6042
18·86	2·00	0·5893
18·86	9·76	0·5289
18·86	21·50	0·4329
18·86	25·97	0·3933
26·37	-	0·6753
26·37	2·55	0·6460
26·37	7·19	0·6016
26·37	13·40	0·5275
26·37	30·87	0·3291
31·45	-	0·6660
31·45	2·81	0·6308
31·45	9·20	0·5505
31·45	11·47	0·5244
31·45	19·35	0·4294
41·59	-	0·5596
41·59	3·02	0·5237
41·59	7·00	0·4702
41·59	11·47	0·4164
41·59	12·50	0·3994

TABLE XVI. - VISCOSITY OF POTASSIUM CARBONATE SOLUTIONS IN A SOLUTION OF POTASSIUM HYDROXIDE AT 25° AND 50°C.

Wt.-%KOH	Wt.-%K_2CO_3	$\eta_{25°}$	$\eta_{50°}$	$d_{4°}^{25°}$	$d_{4°}^{50°}$
28·58	-	2·0975	1·2955	1·2791	1·2644
28·58	2·41	2·2230	1·3570	1·2947	1·2807
28·58	8·14	2·5916	1·5685	1·3309	1·3177
28·58	14·6	3·0946	1·8229	1·3689	1·3520
28·58	21·3	4·1209	2·3554	1·4243	1·4112
31·45	-	2·2786	1·3953	1·3080	1·2964
31·45	2·81	2·5163	1·5254	1·3247	1·3103
31·45	9·20	3·0707	1·8108	1·3669	1·3449
31·45	19·35	4·1197	2·3506	1·4270	1·4139

TABLE XVII. - ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF POTASSIUM CARBONATE AND POTASSIUM BICARBONATE IN THE PRESENCE OF SUCROSE

	Normality	15°Brix sucrose		Normal sucrose	
		$10^5\kappa$	Λ	$10^5\kappa$	Λ
K_2CO_3	0·01	75·6	75·6	57·4	57·4
	0·02	146·3	73·2	108·6	54·3
	0·05	349·1	69·8	249·5	49·9
$KHCO_3$	0·01	71·0	71·0	55·1	55·1
	0·02	138·6	69·3	107·6	53·8
	0·05	333·4	66·7	255·4	51·1

where b is the ratio of the mobilities of the hydroxyl and potassium ions, and c_0 and c_1 are respectively the initial and final concentrations of the solution, the amount of electric current needed to produce a given concentration of potassium hydroxide by the electrolysis, through a porous diaphragm, of a potassium carbonate solution may be found. Within the concentration range 10–30g. of potassium carbonate per 100ml. and the temperature range 20°-70°, A varies from 33•9 to 78•0.[155]

The magneto-optical rotation of the plane of polarization (Faraday effect) by aqueous salt solutions has been measured. The results for potassium carbonate and potassium bicarbonate solutions, together with the derived Verdet constants, are listed in Table XVIII.[156]

TABLE XVIII. - MAGNETO-OPTICAL DATA FOR AQUEOUS POTASSIUM CARBONATE AND POTASSIUM BICARBONATE AT 0°C. AND λ = 5460A.

Wt.-%	$d_{4^\circ}^{0^\circ}$	D_2/D_1	V	M
K_2CO_3				
47•79	1•5114	1•1164	0•0173	3•48
$KHCO_3$				
17•22	1•1214	1•0214	0•0158	2•68

In this table D_2/D_1 is the rotation of the solution relative to the rotation of water at 0°, for the same current and layer thickness: V is the Verdet constant: and M is the relative molecular rotation of the solute when the molecular rotation of water is taken as unity.

The Raman line corresponding to the absorption line at 9•0μ is strongly excited in the scattered radiation from aqueous potassium carbonate; Raman lines corresponding to the absorption lines at 14•16μ, 11•4μ and 6•7μ appear only faintly. These infra-red absorption lines correspond to the classically calculated frequencies of the carbonate ion.[157,157a] The magnitude of the Raman shifts is almost independent of the nature of the cation and is very similar for solutions containing the ions CO_3'', HCO_3' and NO_3'.[158] For example, in a normal solution of potassium carbonate, the mean shift is 1066•5 cm.$^{-1}$ as compared with 1064•8cm.$^{-1}$ for sodium carbonate.[159] Regarding the intensity of this line, taking $J_{\text{Raman}}/J_{\text{Primary}}$ for the line excited by 4358A. in benzene as 100, we obtain[160] J_R/J_P = 14.

Chemical Properties

The reaction between chlorine and solid potassium carbonate has been studied over the temperature range 200°-600°. The main reaction was:-[161]

$$2K_2CO_3 + 2Cl_2 \rightarrow 4KCl + 2CO_2 + O_2.$$

The reaction is more difficult than with sodium carbonate and there is less formation of the perchlorate by a side reaction.[162]

Gaseous sulphur trioxide reacts with solid anhydrous potassium carbonate at 40°, according to the equation:-

$$K_2CO_3 + 3SO_3 \rightarrow K_2S_3O_{10} + CO_2.$$

In the reaction with sodium carbonate under similar conditions $Na_2S_2O_7$ is formed.[163] An equimolar mixture of potassium carbonate and barium sulphate, heated to 600° for five minutes, showed 22•5% conversion to potassium sulphate, the heat of reaction being 9 g.-cal. Replacement of the barium sulphate by lead sulphate gives 40•9% conversion to potassium sulphate, with a heat of reaction of 7 g.-cal.[164] Potassium carbonate lowers the lead oxide-silica eutectic from 675° to 580°, dissolving without decomposition.[165]

A mixture of potassium carbonate, alumina and silica heated in a tungsten spiral, emits K^+ ions at 750° to 800°. The ionization potential is related to the heat of formation of K_2O.[166]

In the system potassium carbonate-potassium chromate the equilibrium temperatures of solidus and liquidus and the corresponding compositions are recorded in Table XIX.[167]

TABLE XIX. - SOLIDUS-LIQUIDUS TEMPERATURES IN THE SYSTEM POTASSIUM CARBONATE-POTASSIUM CHROMATE

Wt.-% K_2CO_3	t, liquidus	t, solidus
100	893	893
90	860	830
80	830	804
70	802	786
60	781	781(minimum)
50	808	-
40	835	804
30	864	824
20	900	875
10	940	920
0	975	975

Aqueous solutions of potassium carbonate are slowly decomposed on boiling. For example, a 0·2N. solution boiled under reflux for 5-7 days in a current of air or steam (to remove carbon dioxide as formed) showed 65% decomposition. The extent of decomposition is stated to be proportional to the square root of the time of boiling, as the following Table shows.[168]

TABLE XX. - DECOMPOSITION OF POTASSIUM CARBONATE (0·2N.) SOLUTION ON BOILING UNDER REFLUX

Time, mins.	CO_2 elimin'd		K(%decomp./mins.$^{1/2}$)
	g.	%	
80	0·0126	7·16	0·801
330	0·0336	14·9	0·82
900	0·0562	25·4	0·846
1355	0·0718	32·9	0·89
1620	0·0778	35·2	0·875
2380	0·0912	41·2	0·845
3050	0·1008	48·75	0·88
3810	0·1096	49·5	0·802
5250	0·1184	53·45	0·738
5960	0·1247	56·3	0·73
6675	0·1315	59·4	0·72
7380	0·1375	62·1	0·73
8180	0·1433	64·7	0·715

The reaction:-

$$K_2CO_3 + CaCl_2 \rightarrow CaCO_3 + 2KCl$$

has been investigated. With normal solutions of reactants at 30°, calcium carbonate in the form of 'vaterite' is obtained; this remains stable only if ethanol also is present (to the extent of 10%), and if the precipitate is separated rapidly, washed with ethanol and ether, and dried.[169]

Double decomposition between solutions of potassium carbonate and magnesium sulphate, at the boiling point, leads to several different magnesium carbonates according to the conditions; the various forms have been studied.[170] When concentrated solutions of potassium carbonate and magnesium chloride are slowly brought into contact, a membrane of the type $MgCl_2$:K_2CO_3 = 2:3 (approximately) is formed.[171,172]

The reciprocal systems Na,K || CO_3,X, where X = F′, Cl′, Br′ and I′, have been studied.[173] The systems are represented in Figs. 2, 3, 4 and 5, details

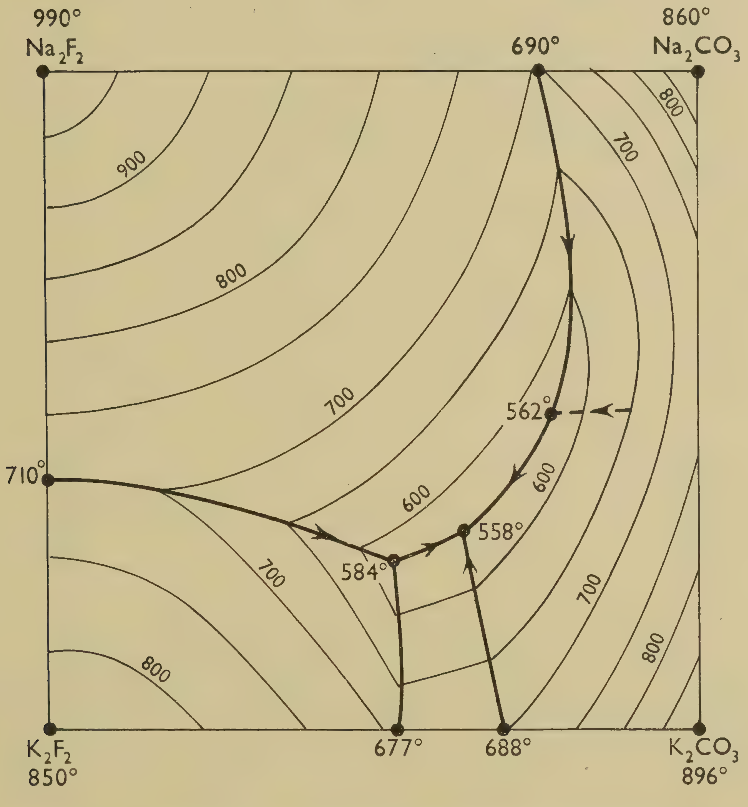

FIG. 2. THE QUATERNARY SYSTEM: K_2CO_3–Na_2CO_3–KF–NaF

of individual systems being as follows:-

Na,K || F′,CO_3. Four binary systems express the results of the study of this system:

K_2CO_3–KF, eutectics occur at 688° and 677° with compositions 70%K_2CO_3 and 57%K_2CO_3 respectively; the intermediate compound is K_2CO_3,KF.

K_2CO_3–Na_2CO_3, complete range of solid solutions.

Na_2CO_3–NaF, simple eutectic at 690° and composition 75%Na_2CO_3.

KF–NaF, eutectic at 710°, 60%KF.

K,Na || Cl′,CO_3. This system may be interpreted in terms of four binary systems:

NaCl–KCl and Na_2CO_3–K_2CO_3, show unbroken ranges of solid solutions.

NaCl–Na_2CO_3, a simple eutectic occurs at 638°, and composition 42%NaCl.

K_2CO_3–KCl, simple eutectic at 623° and 56%K_2CO_3.

The stable diagonal Na_2CO_3–KCl shows a simple eutectic at 588° and 38·5%

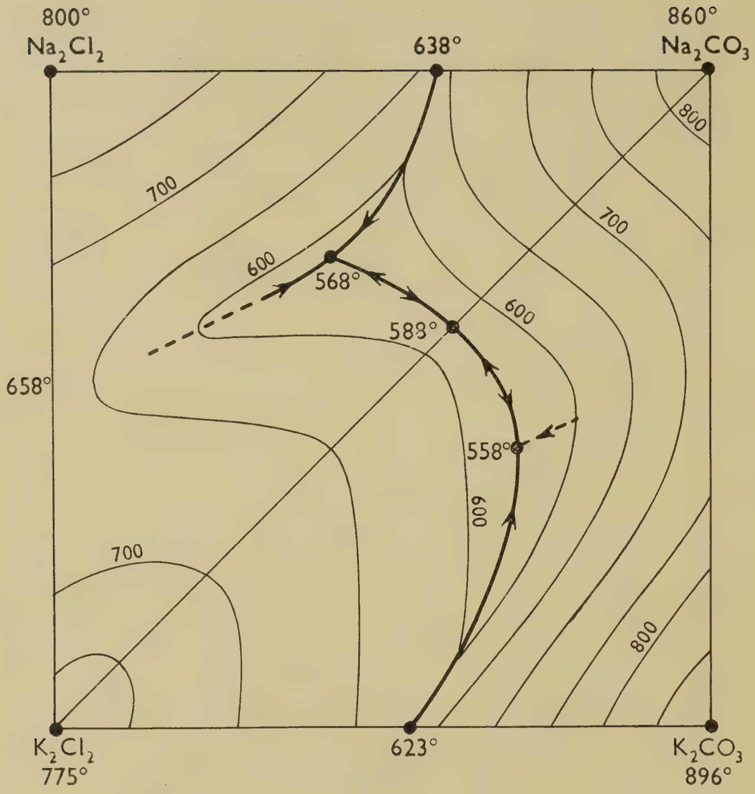

FIG. 3. THE QUATERNARY SYSTEM K_2CO_3-Na_2CO_3-KCl-NaCl

KCl. Two ternary eutectics are observed: one at 558° and composition 18% K_2CO_3, 27%KCl and 55%Na_2CO_3, the other at 568° and composition 28·5%NaCl, 29%KCl and 42·5%Na_2CO_3.

K,Na ‖ Br,CO_3. This system shows two fields of solid solutions, NaBr-KBr, and Na_2CO_3-K_2CO_3 with a ternary eutectic at 575° of composition 32%Na_2CO_3, 32%KBr, 36%NaBr.

The binary systems KBr-K_2CO_3 and NaBr-Na_2CO_3 show simple eutectics at 617° and 613°, with compositions 50%K_2CO_3 and 54%Na_2CO_3. The stable diagonal KBr-Na_2CO_3 shows intersection at 600° with the phase boundary.

K,Na ‖ I,CO_3. No ternary eutectic is observed; the binary systems K_2CO_3-Na_2CO_3 and KI-NaI show unbroken ranges of solid solutions with minima at 712° and 574° respectively.

The binary system NaI-Na_2CO_3 forms a simple eutectic at 588° and 66%Na_2CO_3, whereas the system K_2CO_3-KI forms a eutectic at 612° and 40%K_2CO_3.

The stable diagonal K_2CO_3-NaI intersects the phase boundary at 563° and touches it at 610°.

For the reaction within this system:-

$$2NaCl + K_2CO_3 \rightarrow 2KCl + Na_2CO_3,$$

the heat content change in the forward direction is -7·3g.-cal.[174]

The ternary system K_2CO_3-Na_2CO_3-$BaTiO_3$ has been investigated at temperatures up to 1200°. There are two regions of crystallization: a small

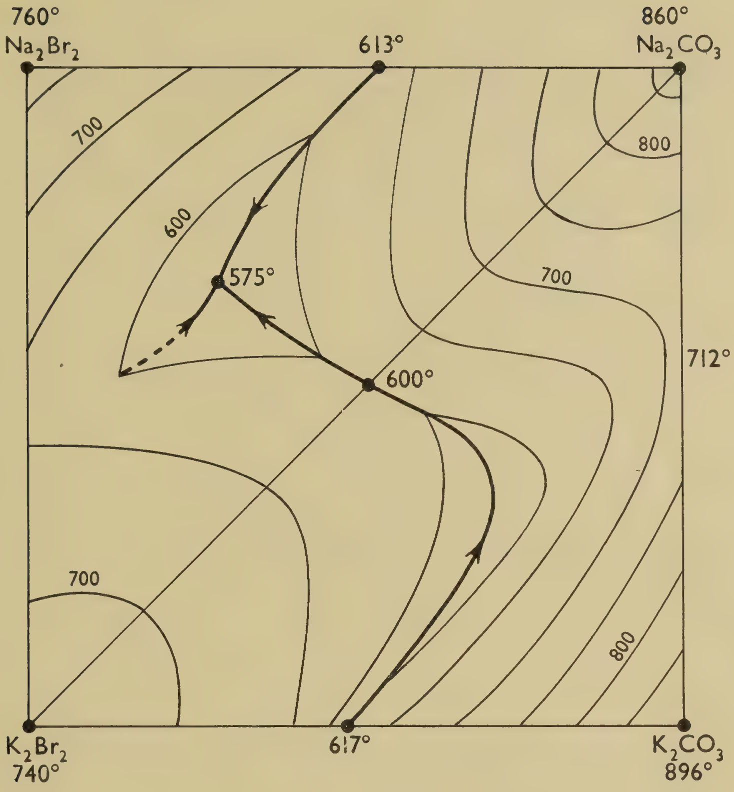

FIG. 4. THE QUATERNARY SYSTEM K_2CO_3–Na_2CO_3–KBr–NaBr

region, 1•27% of the total area, where solid solutions of sodium and potassium carbonates crystallize out, and the remainder where the stable phase is barium titanate. The boundary between the two regions extends from 826° and approximately 1% $BaTiO_3$–99%Na_2CO_3 to an invariant minimum at 700° of composition 60%Na_2CO_3–40%K_2CO_3, rising to 873° with approximate composition 2%$BaTiO_3$–98%K_2CO_3.[175,176]

Considering now systems in aqueous solution, that of K_2CO_3–$KHCO_3$–H_2O has been exhaustively studied. Solubility measurements in this system at 25° and 36° yield the results shown in Table XXI.[177]

TABLE XXI. - SOLUBILITY STUDIES OF THE SYSTEM K_2CO_3–$KHCO_3$–H_2O AT 25° AND 36°

25° Isotherm					
Satd. soln.		$d^{25°}_{4°}$	Original complex		Solid phases
%$KHCO_3$	%K_2CO_3		%$KHCO_3$	%K_2CO_3	
26•55	0	1•180	–	0	$KHCO_3$
19•31	10•0	1•228	28	9	$KHCO_3$
15•45	16•98	1•272	25	15	$KHCO_3$
12•19	23•36	1•316	25	20	$KHCO_3$
7•35	34•71	1•402	20	30	$KHCO_3$
4•44	43•89	1•484	17	38	$KHCO_3$

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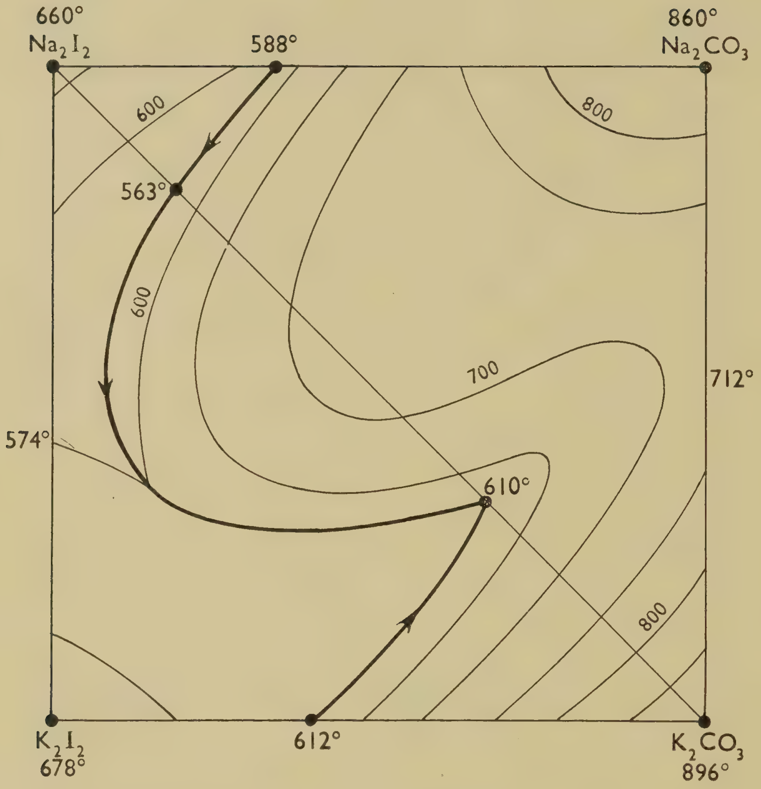

FIG. 5. THE QUATERNARY SYSTEM K_2CO_3-Na_2CO_3-KI-NaI

TABLE XXI (continued)

25° Isotherm					
Satd. soln.		$d_{4°}^{25°}$	Original complex		Solid phases
%$KHCO_3$	%K_2CO_3		%$KHCO_3$	%K_2CO_3	
2·21	51·79	1·558	15	50	$KHCO_3 + K_2CO_3, {}^3\!/_2H_2O$
0	52·74	1·555	0	-	$K_2CO_3, {}^3\!/_2H_2O$
36° Isotherm					
29·9	0	-	-	0	$KHCO_3$
14·83	22·92	1·325	25	20	$KHCO_3$
7·86	37·57	1·437	19	33	$KHCO_3$
3·88	51·44	1·565	7	53	$KHCO_3 + K_2CO_3, {}^3\!/_2H_2O$
0	53·66	1·557	0	-	$K_2CO_3, {}^3\!/_2H_2O$

The 25° isotherm for this system is illustrated in Fig. 6.

Investigation of this system at 42° confirms that the only solid phases are $KHCO_3$ and $K_2CO_3, {}^3\!/_2H_2O$; no compound formation takes place. Potassium carbonate, free from potassium bicarbonate, can be crystallized out at this temperature only when the bicarbonate concentration is less than 2·5%.[178] A more complete investigation of this system has been carried out at 5°, 25°, 35°

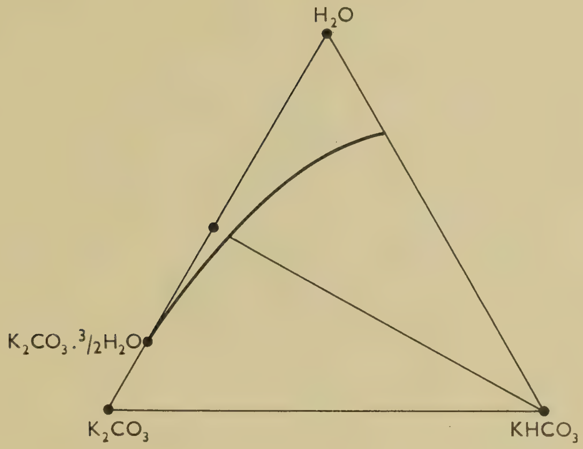

FIG. 6. THE TERNARY SYSTEM: K_2CO_3-$KHCO_3$-H_2O AT 25°C.

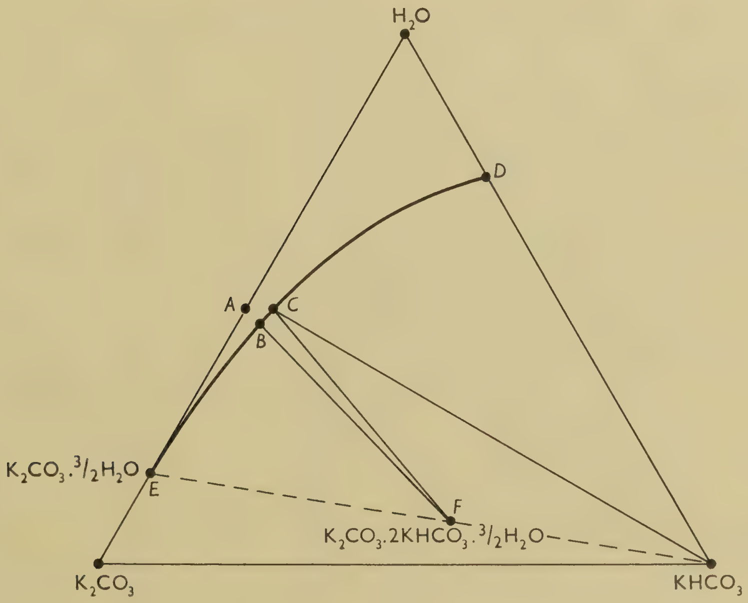

FIG. 7. THE 25° ISOTHERM IN THE TERNARY SYSTEM: K_2CO_3-$KHCO_3$-H_2O

and 50°; the existence is postulated of a double salt, $K_2CO_3,2KHCO_3,{}^3\!/_2H_2O$, stable in contact with the solution from −9•2° to above 50°, but within a very narrow range of concentration.[179] The 25° isotherm is shown in Fig. 7; significant points on this diagram are as follows:-
Point *B*, of composition 51•23%K_2CO_3 and 2•64%$KHCO_3$, defines one phase boundary limit of the double salt; point *C* defines the other limit of this salt, as 49•48%K_2CO_3, 3•33%$KHCO_3$.

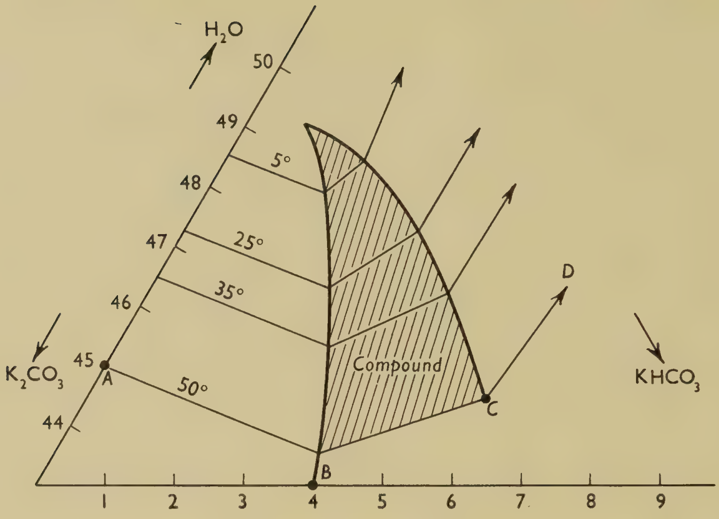

FIG. 8. THE LIMITS OF EXISTENCE OF THE DOUBLE SALT – $K_2CO_3, 2KHCO_3, \frac{3}{2}H_2O$ – AT VARYING TEMPERATURES

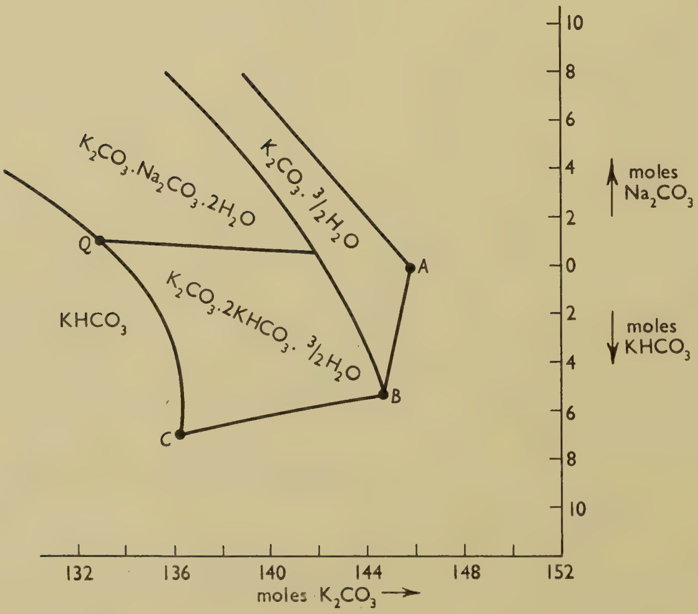

FIG. 9(a). A PORTION OF THE SYSTEM K_2CO_3–$NaHCO_3$–Na_2CO_3–$KHCO_3$–H_2O AT 25°C.

Points *D* and *E* define the limits of the mutual solubility curve. The limits of existence of the double salt vary with temperature, as shown in Fig. 8.[179]

In the system K_2CO_3–$KHCO_3$–Na_2CO_3–$NaHCO_3$–H_2O a study has been made

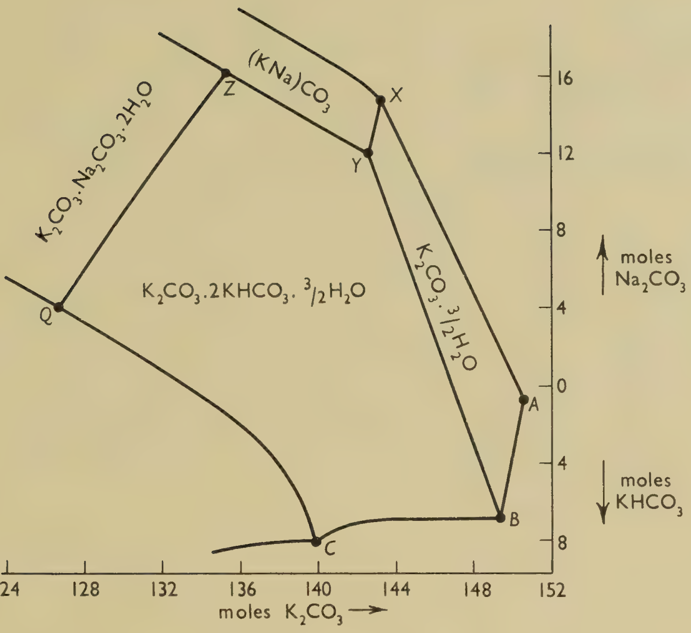

FIG. 9(b). THE SAME SYSTEM AT 35°C.

of the potassium-rich area at 25° and at 35°. Figs. 9a and 9b illustrate the results; the significant points are given in Table XXII.[180,181]

TABLE XXII. - SIGNIFICANT POINTS IN THE PHASE-DIAGRAMS ILLUSTRATED IN FIGS. 9a AND 9b

25° Isotherm					
Wt.-%K_2CO_3	Satd. soln.		Density	Point in Fig. 9a	Solid phases
	$KHCO_3$	Na_2CO_3			
52·77	-	-	1·559	A	$K_2CO_3,{}^3/_2H_2O$
51·23	2·64	-	1·563	B	K_2CO_3 + D.S.
49·48	3·33	-	1·545	C	D.S. + $KHCO_3$
50·05	-	0·38	1·553	Q	D.S. + $KHCO_3$ + T.S.
51·80	-	0·15	1·566	Z	D.S. + T.S. + $K_2CO_3,{}^3/_2H_2O$
35° Isotherm					
Wt.-%K_2CO_3	Satd. soln.		Density	Point in Fig. 9b	Solid phases
	$NaHCO_3$	Na_2CO_3			
53·56	-	-	1·560	A	$K_2CO_3,{}^3/_2H_2O$
51·68	-	-	1·573	B	$K_2CO_3,{}^3/_2H_2O$ + D.S.
49·51	-	-	1·556	C	D.S. + $KHCO_3$
48·42	3·58	1·12	1·547	Q	D.S. + $KHCO_3$ + T.S.
48·62	1·38	4·25	1·568	Z	D.S. + T.S. + $KNaCO_3$

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TABLE XXII (continued)

35° Isotherm					
Wt.-% K_2CO_3	Satd. soln.		Density	Point in Fig. 9b	Solid phases
	$NaHCO_3$	Na_2CO_3			
50·07	–	4·19	1·571	X	$KNaCO_3 + K_2CO_3,\frac{3}{2}H_2O$
50·37	1·19	3·28	1·576	Y	$KNaCO_3 + K_2CO_3,\frac{3}{2}H_2O$ + D.S.

D.S. = double salt $K_2CO_3,2KHCO_3,\frac{3}{2}H_2O$
T.S. = tetragene salt $K_2CO_3,Na_2CO_3,2H_2O$

The system K_2CO_3–Na_2CO_3–H_2O has been studied over a wide range of temperature. Above −6·2°, the only stable hydrate is $K_2CO_3,\frac{3}{2}H_2O$, and below this temperature, $K_2CO_3,6H_2O$. Within the range 20° to 34° a continuous series of ternary solid solutions is in equilibrium with liquid solutions of certain concentrations. These solid solutions are of the type $(K_2, Na_2)CO_3,6H_2O$, the atomic ratio K/Na varying from 1·14 to 0·48. Above 25·12° there exists in contact with solutions rich in potassium carbonate an anhydrous double salt, K_2CO_3,Na_2CO_3, the stability of which increases with increasing temperature. The 25° isotherm is shown in Fig. 10, the significant points of which are listed in Table XXIII.[182]

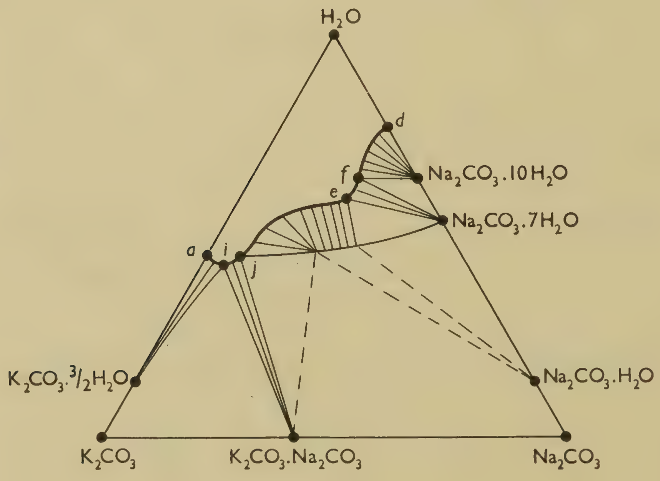

FIG. 10. THE TERNARY SYSTEM: K_2CO_3–Na_2CO_3–H_2O AT 25°

In the same system a transition point $Na_2CO_3,3H_2O \rightarrow Na_2CO_3,H_2O$ is observed at 39·8° C.[183]

Mutual solubility curves for the ternary system sodium bicarbonate–potassium bicarbonate–water at atmospheric pressure and at 20°, 25° and 30° are shown in Fig. 11. No evidence has been found for the existence of hydrates, double salts or solid solutions.[184]

The systems $NaHCO_3$–$KHCO_3$–H_2O and Na_2CO_3–K_2CO_3–H_2O have been investigated at temperatures down to −37°, with the object of separating the components.[185] The existence of a double salt, $Na_2CO_3,K_2CO_3,24H_2O$,[185a]

TABLE XXIII. - SIGNIFICANT POINTS IN THE PHASE DIAGRAM ILLUSTRATED IN FIG. 10 (25°C.)

Wt.-% soln.		Density	Original complex		Point in Fig. 10	Solid phases
H_2O	Na_2CO_3		$\%H_2O$	$\%Na_2CO_3$		
47·2	0	–	–	–	a	$K_2CO_3,\frac{3}{2}H_2O$
46·6	5	1·555	30·0	18·0	b	$K_2CO_3,\frac{3}{2}H_2O$ + S.S.
61·5	22·7	1·395	59	26	e	S.S. + $Na_2CO_3,7H_2O$
64·2	23·3	1·368	63	28	f	$Na_2CO_3,7H_2O + Na_2CO_3,10H_2O$
77·8	22·5	–	–	–	d	$Na_2CO_3,10H_2O$

S.S. = solid solution of type $(Na_2, K_2)CO_3,6H_2O$

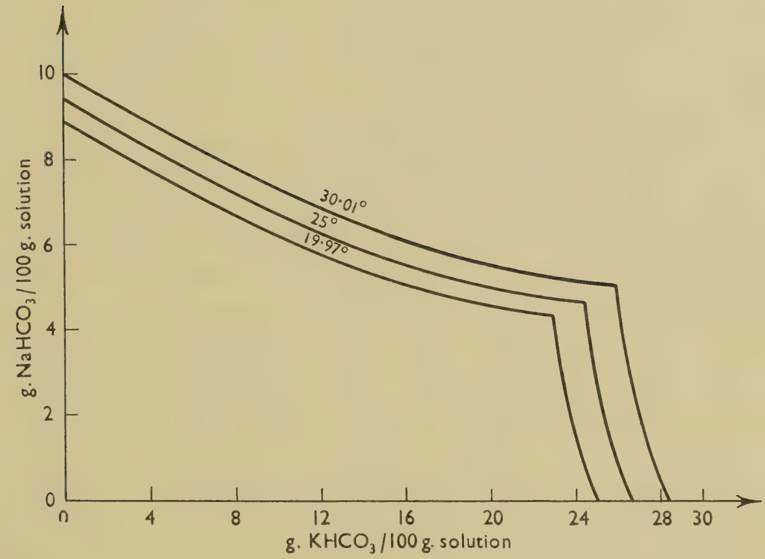

FIG. 11. MUTUAL SOLUBILITY CURVES FOR $KHCO_3$ AND $NaHCO_3$ IN WATER AT VARYING TEMPERATURES

could not be confirmed. The mixed carbonate system has also been studied at high temperatures (up to 200°), and separation by isothermal evaporation investigated.[186] Conditions for the crystallization of Na_2CO_3,K_2CO_3 from aqueous solutions, and its thermal stability, have been examined.[187]

The ternary system potassium carbonate-potassium sulphate-water has been examined at 25°C. The solubility of potassium sulphate in g. per 100g. of saturated solution decreases from 10·7 in pure water to 0·03 in saturated solutions of potassium carbonate. Solid solution formation does not occur to any measurable extent. The full analysis of this system is expressed by Fig. 12 and Table XXIV.[188]

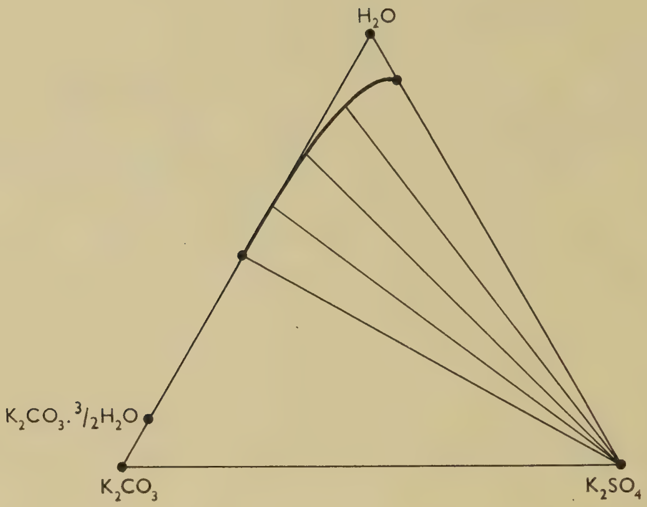

FIG. 12. THE 25° ISOTHERM IN THE TERNARY SYSTEM K_2CO_3–K_2SO_4–H_2O

TABLE XXIV. - SOLUBILITY RELATIONSHIPS IN THE SYSTEM K_2CO_3–K_2SO_4–H_2O AT 25°C.

Original complex		Satd. soln.		Density	Solid phases
Wt.-%K_2SO_4	Wt.-%K_2CO_3	Wt.-%K_2SO_4	Wt.-%K_2CO_3		
–	–	10·7	–	1·083	K_2SO_4
21·8	4·6	6·5	5·5	1·103	K_2SO_4
17·2	8·3	4·9	9·4	1·122	K_2SO_4
17·1	14·1	2·8	16·4	1·170	K_2SO_4
13·7	20·4	1·5	23·2	1·230	K_2SO_4
14·6	30·1	0·3	35·0	1·348	K_2SO_4
8·1	41·5	0·08	45·1	1·465	K_2SO_4
16·6	40·6	0·03	48·6	1·506	K_2SO_4
8·4	51·6	0·03	52·8	1·557	$K_2SO_4 + K_2CO_3, {}^3/_2H_2O$
–	–	–	52·8	1·557	$K_2CO_3, {}^3/_2H_2O$

The mutual solubilities of potassium carbonate and potassium chloride have been determined within the ternary system K_2CO_3–KCl–H_2O. The results at the experimental temperatures are given in Table XXV, and the separation of the two salts is considered in terms of their relative solubilities.[189]

TABLE XXV. - MUTUAL SOLUBILITIES IN THE SYSTEM K_2CO_3–KCl–H_2O

t°	Wt.-%K_2CO_3	Wt.-%KCl
20	51·9	0·8
30	52·22	1·03
50	53·63	1·40
70	56·06	2·00
84	57·16	2·21
100	59·44	2·48
124·5	65·33	2·68

The system K,Na || Cl,CO_3 || H_2O, has been investigated at 25°C. The composition of the saturated solution, and of the solid phase in equilibrium therewith, is recorded in Table XXVI.[190]

TABLE XXVI. - EQUILIBRIUM IN THE SYSTEM K,Na || Cl,CO_3 || H_2O AT 25°C.

G. per 100g. of water in satd. soln.				Solid phases
Na_2CO_3	K_2CO_3	NaCl	KCl	
28	-	-	-	$Na_2CO_3, 10H_2O$
-	-	35·66	-	NaCl
-	-	-	36·97	KCl
-	113·57	-	-	$K_2CO_3, \frac{3}{2}H_2O$
10·89	104·18	-	-	$K_2CO_3, \frac{3}{2}H_2O + NaKCO_3, 6H_2O$
35·57	30·44	-	-	$Na_2CO_3, 7H_2O + NaKCO_3, 6H_2O$
35·63	18·96	-	-	$Na_2CO_3, 7H_2O + Na_2CO_3, 10H_2O$
25·97	-	23·51	-	$NaCl + Na_2CO_3, 10H_2O$
-	-	29·88	16·29	NaCl + KCl
-	110·68	-	2·07	$K_2CO_3, \frac{3}{2}H_2O + KCl$
27·45	-	15·81	13·78	$Na_2CO_3, 10H_2O + NaCl + KCl$
27·03	25·79	10·59	-	$Na_2CO_3, 10H_2O + Na_2CO_3, 7H_2O + KCl$
27·86	29·78	8·55	-	$Na_2CO_3, 7H_2O + Na_2CO_3, 6H_2O + KCl$
11·02	102·5	-	1·82	$NaKCO_3, 6H_2O + K_2CO_3, \frac{3}{2}H_2O + KCl$
27·82	36·29	-	-	$NaKCO_3, 6H_2O$
25·79	33·64	-	9·78	$NaKCO_3, 6H_2O + KCl$
38·65	-	-	22·08	$Na_2CO_3, 10H_2O + KCl$

The results of a similar investigation of the system K,Na || SO_4,CO_3 || H_2O are summarized in Table XXVII.[190]

TABLE XXVII. - EQUILIBRIUM IN THE SYSTEM K,Na || SO_4,CO_3 || H_2O AT 25°

G. per 100g. water in satd. soln.				Solid phases
Na_2CO_3	K_2CO_3	Na_2SO_4	K_2SO_4	
29·78	-	-	-	$Na_2CO_3, 10H_2O$
-	-	27·94	-	$Na_2SO_4, 10H_2O$
-	-	-	12·08	K_2SO_4
-	113·57	-	-	$K_2CO_3, \frac{3}{2}H_2O$
10·89	104·18	-	-	$K_2CO_3, \frac{3}{2}H_2O + KNaCO_3, 6H_2O$
35·57	30·48	-	-	$Na_2CO_3, 7H_2O + KNaCO_3, 6H_2O$
35·63	18·96	-	-	$Na_2CO_3, 7H_2O + Na_2CO_3, 10H_2O$
27·44	-	24·06	-	$Na_2SO_4, 10H_2O + Na_2CO_3, 10H_2O$
-	-	30·98	9·34	$Na_2SO_4, 10H_2O + K_3Na(SO_4)_2$
-	-	6·86	13·31	$K_2SO_4 + K_3Na(SO_4)_2$
26·09	3·58	25·46	-	$Na_2CO_3, 10H_2O + Na_2SO_4, 10H_2O + K_3Na(SO_4)_2$
33·74	7·37	-	6·30	$K_2SO_4 + Na_2CO_3, 10H_2O + K_3Na(SO_4)_2$
35·63	18·50	-	1·45	$K_2SO_4 + Na_2CO_3, 10H_2O + Na_2CO_3, 7H_2O$
35·35	27·07	1·01	-	$K_2SO_4 + NaKCO_3, 6H_2O + Na_2CO_3, 7H_2O$
10·83	103·72	-	1·36	$K_2SO_4 + NaKCO_3, 6H_2O + K_2CO_3, \frac{3}{2}H_2O$

Solubility curves have been constructed for the system K_2CO_3-$NaClO_3$-water at 24·2° and 40°. At the former temperature, solid phases found were $KClO_3$, $NaClO_3$, $Na_2CO_3,7H_2O$, $Na_2CO_3,10H_2O$, $K_2CO_3,2H_2O$ and $K_2CO_3,Na_2CO_3,6H_2O$. In the course of the investigation, a new hydrate, $Na_2CO_3,K_2CO_3,24H_2O$, was found, stable at -6°.[191]

In the system potassium carbonate–calcium hydroxide–potassium hydroxide–calcium carbonate–water, the reaction $Ca(OH)_2 + K_2CO_3 \rightarrow 2KOH + CaCO_3$ takes place with a 98% yield in 0·92 molar potassium carbonate solution; but only a 46% yield is obtained with 9·45 molar solution.[192]

The system potassium carbonate–ammonia–water has been studied at 0°, 18° and 25°. Two liquid phases are obtained which, when saturated with salt, have a critical solution temperature above 155°. The vapour pressure of the univariant four-phase system was investigated from 0° to 30°; it is 76cm. Hg at 22·5°. The stable hydrate of potassium carbonate was found to be $K_2CO_3,2H_2O$; the system is illustrated in Fig. 13.[193]

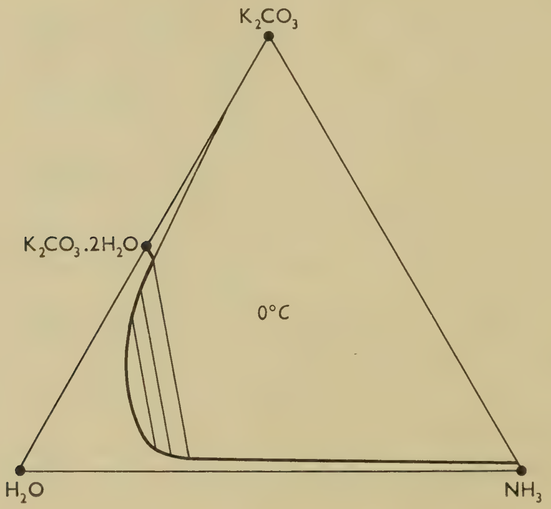

FIG. 13. THE TERNARY SYSTEM: K_2CO_3–NH_3–H_2O AT 0°C.

When anhydrous potassium carbonate is added to an aqueous solution of ammonia, of any concentration and below 20°, two layers form; if the heat of dilution is not removed by cooling, the temperature may rise above this value. The upper layer contains 1% of the ammonia; the lower layer contains less than 1% of the carbonate.[194] Continued passage of ammonia through the solution results in the separation of a solid phase, $K_2CO_3,2H_2O$.[195]

The reaction: $MgCO_3 + KHCO_3 \rightarrow MgKH(CO_3)_2$ has been studied. The maximum yield is obtained by cooling the reaction mixture to 0°. The product crystallizes with four molecules of water of crystallization, forming the well-known Engel's salt.[196]

Boyle's observation of 1680, that a yellow solution was obtained from powdered sulphur and anhydrous potassium carbonate in alcohol at room temperature, has been verified. The absence of a Tyndall effect shows that the solution is not colloidal; on acidification, hydrogen sulphide and sulphur are obtained. Potassium polysulphides are present in the solution, and agitation with air yields potassium thiosulphate.[197]

The distribution of a number of anions X, in the system potassium carbonate–water–ethanol–KX, has been measured. The results are given as the ratio of the concentration of KX in water to that in ethanol:-[198]

X =	HPO_4''	Cl′	NO_3'	ClO_3'	Br′	I′	CNS′
c_w/c_e =	92	2·2	2·2	2·1	1·1	0·34	0·17

The ternary equilibrium sucrose–water–potassium carbonate has been investigated at 30°. The addition of potassium carbonate to the system first lowers, then suddenly increases, the solubility of sucrose; sodium carbonate, in a similar system, has a smaller effect. A marked increase in viscosity is observed. The stable form of potassium carbonate in this system, at 30°, is $K_2CO_3, \frac{3}{2}H_2O$.[199]

Potassium carbonate forms addition compounds with several phenyl alkyl ethers, of general formula K_2CO_3,2ROR′, which have been isolated.[200]

The ternary systems potassium carbonate–water–glycol and potassium carbonate–water–dioxan have been studied and are illustrated in Fig. 14.

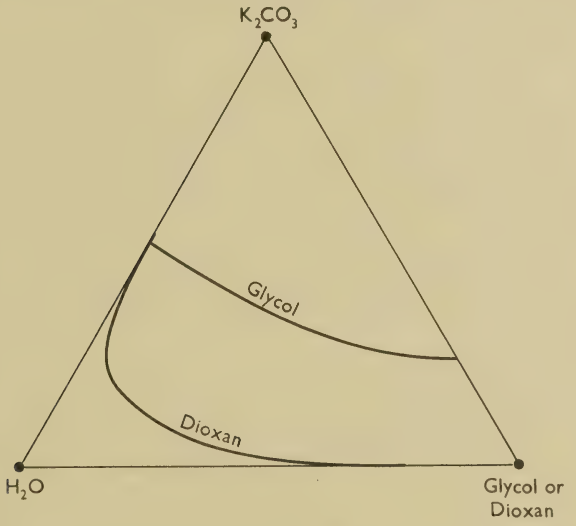

FIG. 14. THE TERNARY SYSTEMS: K_2CO_3–H_2O-GLYCOL, K_2CO_3–H_2O-DIOXAN AT 25°C.

Salting out of the dioxan was observed with potassium carbonate and other electrolytes; of thirty-one salts tried, including potassium carbonate, none salted out ethylene glycol.[201]

In Fig. 15, the binodal curves are given for the systems potassium carbonate–water–*iso*propyl alcohol and potassium carbonate–water–*tert.*-butyl alcohol.[202,203]

Some chemical properties of potassium carbonate of particular interest to the glass industry have been investigated. On heating a mixture of potassium carbonate, boron trioxide and quartz, reaction commences at about 500°, well below the melting-point of any of the components. Below 700° no insoluble potassium borosilicates are formed, but they are increasingly present as the temperature rises to 900°. The composition of the equilibrium solid $xK_2O, yB_2O_3, zSiO_2$ changes with change of temperature.[204] Reactions in the binary systems potassium carbonate–silica, and potassium carbonate–triplumbic tetroxide, have been studied at temperatures up to 1200°. The lead oxide decomposes at 500°–600°; potassium silicate is rapidly formed at about 800°. The product is not completely homogeneous below 1200°. Water-solubility becomes negligible at 800°, but acid-solubility decreases progressively with increase in temperature in the complete system K_2O–PbO–SiO_2.[205]

The use of potassium carbonate in the glass industry has been reviewed, and appears to be limited to the production of decorative, ophthalmic and optical glasses.[206] The substitution of other alkalis for potash in lead oxide

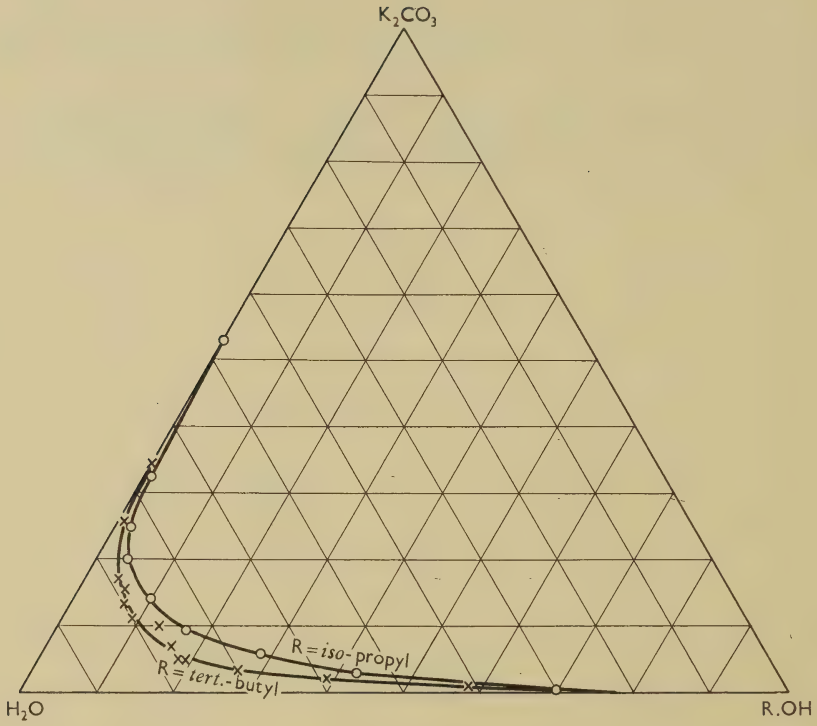

FIG. 15. THE TERNARY SYSTEMS: K_2CO_3-H_2O-*iso*PrOH, K_2CO_3-H_2O-*tert*-BuOH AT 25° C.

glasses and its effect upon their properties have been considered.[207] A readily fusible potassium carbonate for use in glass-making is obtained by adding a small amount of boric acid or borax.[208]

The action of potassium carbonate on bottle-glass has been studied; both lead and arsenic present in the glass are slowly absorbed.[209,210] Standards of durability for glass containers have been suggested.[211]

In gold-ruby glass, which is the most satisfactory as regards colour permanence during lamp-working, replacement of sodium carbonate by potassium carbonate decreases the ruby colour.[212]

Analysis

A flame photometric method for the determination of sodium in potassium carbonate has been described; if the sodium content is known approximately, it is sufficient to use two comparative solutions, of slightly higher and slightly lower sodium content than the sample. It is essential that the comparative solutions contain also the foreign anions of the sample solution; the accuracy of this method is sufficient for industrial control purposes.[213]

An iron content of the order of 0.0004 to 0.0012% in potassium bicarbonate may be determined thus: 25 to 30g. of sample are dissolved in 100ml. of water, 3 to 8g. of tungsten oxide, WO_3, 7 to 8g. of Rochelle salt, 4g. of glucose and 40mg. of copper as copper sulphate are added, and the solution electrolyzed. The iron present in the copper–tungsten–iron alloy so obtained is determined iodometrically. The method compares favourably with the Holtz–Swalheim method.[214]

Uses

A study has been made of the use of potassium carbonate as an inhibitor of corrosion of stainless steel in electrolyte solutions;[215] on the other hand, potassium bicarbonate is a cause of the corrosion of cast iron and steel vessels during the leaching of solutions in alumina production.[216]

Potassium carbonate, or crude potash from beet 'vinasse', may be converted into fertilizer by admixture with phosphate and a source of nitrogen.[217,218] Potassium carbonate has also been incorporated in the synergistic weed-killing materials.[219]

Phase-rule studies of the system potassium carbonate–water–alcohol–petrol have been made, in connexion with the dehydration of alcohol.[220,221] The dehydration of *iso*amyl alcohol by treatment with anhydrous ethyl alcohol and solid potassium carbonate at 20°, has been investigated.[222] The addition of 1 to 10% of potassium carbonate to tertiary aliphatic halides stabilizes them against decomposition in storage.[223] The ether extracts of liver oils may advantageously be dried over potassium carbonate, as peroxides responsible for the decomposition of vitamin A are thereby destroyed.[224]

Wooden separators for use in lead-acid storage batteries may be protected by impregnating them with a concentrated solution of sodium and potassium carbonates at 55°–90°.[225]

Plastering at temperatures as low as $-32°$ is facilitated by mixing the plaster with potassium carbonate solution of density 1·08: the adhesion is improved.[226] Treatment of the surface of plasterboard with a solution of potassium carbonate saponifies the rosin contained in surface fibres; aqueous plastering compounds may then be applied.[227]

The reactivity of 600°–1000° coke in producer-gas manufacture is improved by treatment of the coal with potassium carbonate solution: 7% of potassium carbonate increases reactivity six times at 700°, and at 900° the gas equilibrium is shifted completely to carbon monoxide.[228]

The reduction of chromite at 1300° by both hydrogen and carbon is accelerated by the addition of 3% of potassium carbonate.[229]

A solution of potassium carbonate has been suggested, as an alternative to the usual calcium chloride–sodium chloride solution, in refrigeration.[230]

Liquid carbon dioxide may be produced by compressing the gas into solution in aqueous potassium carbonate; the gas is then liberated at 270°–280°, and is passed into a condenser where it is liquefied. This process results in a saving of energy, and coal consumption is reduced to 0·7–0·9kg. per kg. of carbon dioxide.[231]

Carbon dioxide and hydrogen sulphide may be removed from gas mixtures by scrubbing with 40% potassium carbonate solution at 250° and 300lb./sq.in. pressure; the used solution may be regenerated.[232]

The addition of from 1 to 8% of potassium carbonate to dry bleaching powders (calcium hypochlorite + sodium tripolyphosphate) reduces considerably the loss of chlorine in storage.[233]

Among many applications of potassium carbonate as a catalyst and as a promoter the following may be mentioned:

Carbon monoxide and hydrogen form *iso*butanol when passed over a copper chromite catalyst at 500° with potassium carbonate as promoter.[234] The formation of imines by interaction of amines and ketones is catalyzed by potassium carbonate.[235] By immersion in a 10% potassium carbonate solution and drying, granular Raney-type catalysts are strongly inhibited as regards

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dehydration; dehydrogenation activity, however, remains unaltered.[236]

Carbon monoxide (8–26%) and hydrogen (68–70%) interact at 305°–350°, and at a pressure of 20–30 atm., to form C_3, and higher, hydrocarbons; with a catalyst composed of mill scale impregnated with potassium carbonate, a conversion of 85% may be obtained.[237]

Potassium carbonate promotes the iron catalyst employed in the synthesis of olefines, esters and alcohols from carbon monoxide and hydrogen.[238-247] It also acts as a promoter to the zinc oxide–cadmium oxide catalyst used in the dehydrogenation of piperazine to pyrazine.[248]

The addition of potassium carbonate to wood charcoal lowers to 650° the temperature at which a practical water-gas reaction occurs.[249-251] A similar catalyst converts a mixture of carbon monoxide and water into formic acid.[252]

Potassium carbonate catalyzes the removal of hydrogen chloride from chlorohydrins to form epoxides.[253] Similarly, brominated fatty acid esters lose hydrogen bromide readily when passed over potassium carbonate at 170°.[234]

The passage of a mixture of hydrocarbon oil and steam, at atmospheric pressure and at 500°–750°, over potassium carbonate, gives a combustible gas containing mainly methane, hydrogen and carbon monoxide.[255]

The vapour phase condensation of furfural and acetaldehyde is catalyzed by potassium carbonate, and a 25·6% yield of 2-furanacrolein is obtained.[256]

'Polyamide' is prepared by heating ϵ-caprolactam in an autoclave with about 2% of potassium bicarbonate for 16 hours at 230°.[257]

The oxidation of carbon black by air, to give a mixture of carbon monoxide and carbon dioxide, is catalyzed by potassium carbonate.[258] The transfer of oxygen in this reaction has been followed using ^{14}C.[259]

Potassium Percarbonates

The action of fluorine on a solution of potassium carbonate gives an oxidizing solution assumed to contain percarbonates;[260] the only well-established electrolytic percarbonate is the potassium salt, $K_2C_2O_6$.[261] In a review of the alkali percarbonates which had been reported previously two potassium percarbonates are recognized, and experimentally confirmed, as follows.[262] The percarbonate $KHCO_4$ is obtained either by saturating an alcoholic suspension of potassium hydrogen peroxide perhydrate ($KOOH,\frac{1}{2}H_2O_2$) with carbon dioxide at a low temperature, or from hydrogen peroxide and potassium monomethyl carbonate, as a fine crystalline precipitate, much less stable than the corresponding sodium salt. This percarbonate liberates much iodine and oxygen from concentrated neutral potassium iodide solution.

From potassium carbonate and hydrogen peroxide in varying proportions below −5° the addition of excess alcohol gave the compounds: $K_2CO_4,2{\cdot}5H_2O$; $K_2CO_4,H_2O_2,1{\cdot}5H_2O$; and $K_2CO_4,2H_2O_2,H_2O$. These evolved oxygen but not iodine from potassium iodide solution in the cold. All three compounds in alcohol absorbed carbon dioxide to form $K_2C_2O_6$ and water. This last percarbonate could be dried in vacuo over phosphoric oxide and liberated both iodine and oxygen from potassium iodide solution. In general, the per-salts of weak acids such as boric, carbonic and silicic show considerable hydrolysis in solution.

The passage of carbon dioxide over granulated potassium peroxide (K_2O_4) at 0° leads to the slow formation of percarbonates.[263] Conversion to K_2CO_4 is almost complete after 980 hours at a flow rate not exceeding 0·2 litres/hour, to prevent spontaneous rise in temperature. This reacts with more carbon dioxide to form $K_2C_2O_6$, and finally $K_2C_2O_5$ is formed, with the liberation of oxygen, after 1300 hours. At 10° $K_2C_2O_6$ is not formed, and at 25° the process consists only of the two steps: $K_2O_4 + CO_2 \rightarrow K_2CO_4 + O_2$ and $K_2CO_4 \rightarrow K_2CO_3 + \frac{1}{2}O_2$.

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SECTION LVII

POTASSIUM NITRATE

By D. S. and MRS. G. M. PAYNE

OCCURRENCE AND HISTORICAL BACKGROUND

Potassium nitrate, commonly known as saltpetre or nitre, occurs native in very limited amounts in many parts of the world,[1] including East and Central India,[2] the Caucasus,[3] Honan and other provinces of China,[4] Central Australia,[5] the north western part of Cape Colony and the Transvaal,[6] and Calabria.[7] In addition, appreciable amounts of potassium nitrate are present in caliche mined in Chile, which is primarily a source of sodium nitrate.[8]

The history of saltpetre has until recently solely followed man's interest in the manufacture and supply of gunpowder, production and sources suffering many upheavals in the course of time, as might be expected with such a strategically important material. Various works refer to its interesting history (see Mellor II, 802, and Thorpe's Dictionary of Applied Chemistry, 3rd Edition, Vol. V, 400, and 4th Edition, Vol. X, 105 and a number of articles[9]). From time to time new historical facts come to light, e.g. the proposal in 1326 to erect a factory in Florence to manufacture the materials for gunpowder.[10]

PRODUCTION, PREPARATION AND FORMATION

The manufacture of potassium nitrate, as described in a large number of patents and papers, makes use of the main potash minerals as starting materials. The methods employed are fully described in Thorpe's Dictionary of Applied Chemistry (*loc. cit.*).

Minerals rich in potassium chloride may be treated either with nitric acid[11] as vapour[12] or in solution,[13] or directly with nitrous gases[14] to give the nitrate together with nitrosyl chloride, the latter being reconverted to nitric acid or nitrous gases for further use. The kinetics and mechanism of the reaction:-

$$3KCl(s) + 4HNO_3(g) \rightarrow 3KNO_3(s) + NOCl(g) + Cl_2(g) + 2H_2O(g)$$

have been studied in detail and it is suggested that water acts as catalyst.[15] The free energy change for the reaction:-

$$2NO_2(g) + KCl(s) \rightarrow KNO_3(s) + NOCl(g)$$

has been calculated to be $-5{\cdot}623$ kg.-cal. at 25°.[16]

Various nitrates[17] including principally those of calcium, ammonium, sodium and aluminium can be used in double decomposition reactions with aqueous solutions of potassium chloride or potassium sulphate minerals, the efficiency of the processes being dependent on the individual phase diagrams for the various systems (q.v.). Many aids to the separation of potassium nitrate are employed, such as lowered temperatures,[18] mixed solvents,[19] flotation techniques[20] and the use of liquid ammonia as a solvent.[21] Separation of potassium nitrate from the reaction mixture of potassium sulphate and nitric acid is readily accomplished.[22] Methods based on a solid reaction between metal nitrates and potassium chloride[23] are also possible, the separation of the potassium being affected by one of the techniques referred to above.

Ion exchange processes using synthetic exchange resins[24] and a variety of mineral exchangers[25] are particularly attractive as a means of converting the chloride or sulphate into the nitrate.

The silicate potash minerals, notably leucite, are readily converted to potassium nitrate by the action of nitric acid.[26]

Potassium nitrate, together with nitrite, is produced when oxides of nitrogen, obtained directly from the Birkeland Eyde process, are passed over finely divided felspar.[27]

When intended primarily for use as a fertiliser, potassium nitrate is often produced along with soluble phosphate, for example, by the treatment of a mixture of potassium sulphate and phosphate rock with nitric acid.[28]

The extraction of potassium from sea water as the nitrate can, it is said, be accomplished by the use of the calcium salt of methylpentanitrodiphenylamine. The precipitated potassium salt treated with nitric acid yields potassium nitrate and the diphenylamine compound, which can be re-cycled.[29]

Potassium tartrate obtained in wastes from the wine industry can be converted to nitrate by treatment with calcium nitrate.[30]

Direct synthesis of potassium nitrate at 900° in 53% yield occurs by the reaction:-[31]

$$2N_2 + 5O_2 + 4KOH \rightarrow 4KNO_3 + 2H_2O$$

Potassium nitrate is among the products obtained when potassium iodide is treated with dinitrogen tetroxide.[32]

The conversion of nitrite to nitrate is effected, in aqueous solution by dinitrogen tetroxide,[33] or in the melt by oxygen in the presence of alkali,[34] and by the use of a rhenium catalyst.[35]

PHYSICAL PROPERTIES

Solid State

The structure of stable ortho-rhombic potassium nitrate, KNO_3 II, was determined by Zachariasen.[36] Lattice constants revised by later workers are shown in Table I.[38]

TABLE I.- LATTICE CONSTANTS OF POTASSIUM NITRATE

Lattice Constants of Potassium Nitrate (in A.)			
	a	b	c
Zachariasen[36]	5·41	9·16	6·42
Edwards[37]	5·44	9·16	6·46
Swanson and Fuyat[38]	5·414	9·164	6·431 at 26°C

The space group is V_h^{16}, and there are 4 'molecules' in the unit cell. The nitrate ion being taken as planar and parallel to the *c* face, the closest oxygen–oxygen distance in this structure is 2·10 A.[37] Crystal details are given in Mellor (II, 808) and the Barker Index of Crystals Vol. I, Part 2, O 309. The effect of dyes on the crystal habit has been discussed.[39] Microscopic examination reveals a further crystalline form, a rhombohedral modification enantiomorphic with KNO_3 II;[40] transformation to this rhombohedral form, KNO_3 I, occurs at 127·7°. The fact that after a cycle of heating and cooling of a single crystal the resulting pseudo-single crystal still contains many of the axial features of the original crystal, is taken as indicating that this transformation at 128° does not involve a change to a completely independent and random aggregate of crystals of an entirely new structure.[41] If a single crystal is heated above 195° (or at a lower temperature if a powdered sample), on cooling it aquires abruptly, at 123°, a mosaic character which it retains until at 113° it changes into the finely divided rhombic form, KNO_3 III.[42,43]

Differences in behaviour of dry and moist samples are reported and a rhombohedral high pressure form has been identified by differential thermal analysis.[44] The unit cell of KNO_3 III contains only one 'molecule', and has a = 4·365A., α = 76°56′, at 120°, with the space group C_{5v}^3.[45] The X-ray powder pattern reported in the ASTMcard 1188 is of KNO_3 II.[46] Powder patterns of KNO_3 III at 115° by Barth,[45] by Finbak and Hassel,[47] and by Kracek, Barth and Ksanda[48] do not agree amongst themselves. A powder pattern of KNO_3 IV recorded at 5000 kg./sq. cm. shows the crystal to be orthorhombic with 18 'molecules' per unit cell, having[49] a_0 = 16·12, b_0 = 10·12, c_0 = 7·75A. The X-ray powder patterns of potassium, lithium, and sodium nitrates and their mixtures have been reported at room temperature and above.[50]

Heat capacity measurements give the transition temperature as 126·8°C.[51] and 127·9 ± 0·1°C.[52] the heat transition being 1218 ± 5g.-cal./mole and the m.p. 334·3 ± 0·1°C. with a heat of fusion of 2300 ± 5g.-cal./mole.[52] The volume change accompanying the transformation of KNO_3 II to KNO_3 I is 0·0049ml./g.[53] The entropy at 298·16°K. is 31·77 ± 0·10g.-cal.deg.$^{-1}$ mole^{-1}.[54] The magnetic susceptibility perpendicular to the plane of the nitrate ion is greater than for directions in the plane.[55] Measurement of magnetic susceptibility at the transition temperature shows only a small effect arising entirely from the movement of atoms and in no way from changes in electronic states.[56] Molecular rotation in crystals of potassium nitrate is complex, and data based on an X-ray powder diagram at 152° are available.[57] Twinning of potassium nitrate occurs under conditions of plastic deformation.[58,59] The principal coefficients of thermal expansion, from X-ray rotation photographs, for orthorhombic potassium nitrate for the temperature range 30° - 100° are 2·35 × 10^{-6} along the a axis, 22·0 × 10^{-6} along the b axis, and 182·6 × 10^{-6} along the c axis.[60] The coefficient of expansion and the density in g./c.c. respectively are, at 18°, 21 × 10^{-5} and 2·098; at −78°, 14 × 10^{-5} and 2·141; at −195°, 7 × 10^{-5} and 2·175.[61] Precision measurements of the density gave 2·1128 g./ml. at 0·0°C. and 2·1005g./ml. at 30·8°.[62] The dielectric constant is 4·5,[63] 4·55 (10° − 23°)[64] or 4·37 (18°).[65] The electrical conductivity of solid potassium nitrate between 240° and 320° varies with the method used for making the experimental bars; the temperature coefficient is, however, the same in all cases, thus at 240° a bar obtained by the solidification of the melt has a conductivity of 6·76 × 10^{-7} ohm^{-1} cm.$^{-1}$, whereas a bar obtained by direct pressing of powdered potassium nitrate has a conductivity of 7·94 × 10^{-7} ohm^{-1}cm.$^{-1}$ and a bar made by pressing a mixture consisting of 37% of potassium nitrate and 63% of sand has a conductivity of 4·24 × 10^{-7} ohm^{-1} cm.$^{-1}$; at 280° the values are 29·1, 33·8 and 18·2 × 10^{-7} ohm^{-1}cm.$^{-1}$ respectively.[66] The electrical conductivities of powdered potassium nitrate measured with an accuracy of ± 10% at 240°, 260°, 280°, 300° and 320° are 18 × 10^{-7}, 20 × 10^{-7}, 100 × 10^{-7} and 230 × 10^{-7} ohm^{-1} cm.$^{-1}$ respectively.[67a] These values have been confirmed by later work.[67] A marked rise in conductivity occurs in passing through the transition point at 129°.[68] The heat capacity (300° − 330°) of potassium nitrate shows a maximum at 319·5°.[69]

Liquid State

The melting point of potassium nitrate varies with the gas surrounding and adsorbed on the crystals; e.g. in helium, m.p. 333·8°; in hydrogen, 333·5°; in neon, 333·2°; in argon, 332·0°; and in carbon dioxide, 331·0°C.,[70] as compared with the normal m.p. 333·0° ± 0·5.[86] The melting point is remarkably low as compared with potassium chloride, a larger entropy of fusion being involved. This is explained by the formation of association complexes in the nitrate melts.[68] The electrical conductivity has been re-measured,[71] at temperatures below and above the melting point; the jump of conductivity on melting is 3000-fold.[68] The specific conductivity in $\text{ohm}^{-1}\,\text{cm.}^{-1}$ from the m.p. up to 410°C. is represented by the equation:-[72]

$$\kappa = 2{\cdot}87 \times 10^{-3}(t - 339) + 0{\cdot}6440\ \text{ohm}^{-1}\,\text{cm.}^{-1}$$

The potential difference required when potassium nitrate is electrolyzed at 370°C. with hydrogen present at the electrode, varies from 0·5 to 0·6 V.[73] Using potassium nitrate at 360°-380°C. as the solvent, the reduction potentials of Ag^{+}, Cd^{2+}, Pb^{2+}, and $Cr_2O_7{}^{2-}$ measured by a polarographic method were −0·03, −0·42, −0·25 and −0·40 V respectively.[74] Studies of the depression of freezing point of molten potassium nitrate by the addition of salts have shown the melt to behave as an ionised solvent, not necessarily completely dissociated.[75,76,77] Values of the refractive index of molten potassium nitrate are given in Table II.

TABLE II. REFRACTIVE INDEX OF MOLTEN POTASSIUM NITRATE

Wavelength	Wagner[78]	Meyer and Heck[79]
A.		
6710	$1{\cdot}396 - 1{\cdot}5 \times 10^{-4}(t - 440)^{*}$	–
6439	–	$1{\cdot}525 - 3{\cdot}12 \times 10^{-4}t^{\blacktriangle}$
6100	$1{\cdot}403 - 1{\cdot}2 \times 10^{-4}(t - 440)^{*}$	–
5983	$1{\cdot}409 - 1{\cdot}3 \times 10^{-4}(t - 440)^{*}$	$1{\cdot}664 - 4{\cdot}00 \times 10^{-4}t^{\blacktriangle}$
5791	$1{\cdot}418 - 1{\cdot}0 \times 10^{-4}(t - 440)^{\dagger}$	$1{\cdot}556 - 5{\cdot}75 \times 10^{-4}t^{\blacktriangle}$
5461	$1{\cdot}424 - 1{\cdot}0 \times 10^{-4}(t - 440)^{\dagger}$	$1{\cdot}538 - 3{\cdot}12 \times 10^{-4}t^{\blacktriangle}$
4360	$1{\cdot}431 - 1{\cdot}1 \times 10^{-4}(t - 440)^{\dagger}$	–

* measured at 340°-550°C.

▲ measured at 320°-440°C.

† measured at 340°-560°C.

The molecular refraction at 336°C. is 13·46 (λ = 6710A.), 13·78 (λ = 0·5893A.), and 14·10 (λ = 0·5461A.).[78] Measurements at 20° intervals in the range 320° - 440°C. suggest that the molecular refraction is almost independent of temperature.[80] The viscosity at 348° is 2·76, and at 542°C., is 1·29 centipoises.[81] Viscosity data confirm that the molten salt is completely ionised,[82] but there is evidence from a break in the plot of temperature against temperature coefficient of viscosity to suggest a structural change at 440°C.[83]

Binary and Ternary Systems

Since the publication of Mellor, II, much information has been published on numerous systems of potassium nitrate with other compounds as indicated in Tables III - V.

TABLE III. BINARY AND TERNARY SYSTEMS CONTAINING POTASSIUM NITRATE

System	Reference	Items of Special Note
KNO_3 – LiOH	(84)	–
KNO_3 – $NaNO_3$	(85) (86) (87)	Electrical conductivity[88] Mechanism of fusion and solidification of mixed crystals consisting of 80% sodium nitrate and 20% potassium nitrate.[89] Mechanical strength of solidified melt.[90]
KNO_3 – $NaNO_2$	(91)	Electrical conductivity[92]
KNO_3 – NaF	(93)	
KNO_3 – NaBr	(94)	

(continued)

TABLE III. (continued)

System	Reference	Items of Special Note
$KNO_3 - KOH$	(95)	–
$KNO_3 - KCl$	(96)	–
$KNO_3 - KBr$	(96)	Electrical conductivity[97]
$KNO_3 - KI$	(98)	–
$KNO_3 - KNO_2$	(99)	–
$KNO_3 - RbNO_3$	(100)	Electrical conductivity[101]
$KNO_3 - Ca(NO_3)_2$	(87) (102)	Electrical conductivity[103] Formation of a glass-like solid with 41%-59% by weight potassium nitrate.[104]
$KNO_3 - Sr(NO_3)_2$	(105)	–
$KNO_3 - Ba(NO_3)_2$	(106) (107)	–
$KNO_3 - BaCl_2$	(108)	–
$KNO_3 - AgNO_3$	(109)	Viscosity[110] Electrical conductivity[110,111]
$KNO_3 - Pb(NO_3)_2$	(112)	Mechanical strength of solidified melt.[90] Density[113] Structure by photomicrophotography after polishing and etching.[114]
$KNO_3 - Cd(NO_3)_2$	(115)	–
$KNO_3 - Na_2Cr_2O_7$	(116)	–
$KNO_3 - K_2Cr_2O_7$	(116)	–
KNO_3 - K tungstate	(117)	–
$KNO_3 - TlBr$	(118)	–
$KNO_3 - TlI$	(98)	–
$KNO_3 - NH_4NO_3$	(119)	–
$KNO_3 - CO(NH_2)_2$	(120)	–
$KNO_3 - LiNO_3 - NaNO_2$	(121)	–
$KNO_3 - LiNO_3 - Ca(NO_3)_2$	(122)	–
$KNO_3 - LiNO_3 - Cd(NO_3)_2$	(123)	–
$KNO_3 - LiNO_3 - TlNO_3$	(124)	–
$KNO_3 - NaNO_3 - Sr(NO_3)_2$	(105)	–
$KNO_3 - NaNO_3 - Ba(NO_3)_2$	(107)	–
$KNO_3 - NaNO_3 - Pb(NO_3)_2$	(125)	–
$KNO_3 - NaNO_3 - NH_4NO_3$	(126)	–
$KNO_3 - RbNO_3 - Cd(NO_3)_2$	(127)	–
$KNO_3 - NaCl - Tl_2SO_4$	(128)	–
$KNO_3 - K_2SO_4 - K_2CrO_4$	(129)	–
$KNO_3 - K_2SO_4 - KCl$	(129a)	–
$KNO_3 - Ca(NO_3)_2 - Ba(NO_3)_2$	(130)	–
$KNO_3 - Sr(NO_3)_2 - Ba(NO_3)_2$	(113) (131)	–
$KNO_3 - AgNO_3 - Cd(NO_3)_2$	(132)	–
$KNO_3 - AgNO_3 - NH_4NO_3$	(133)	–
$KNO_3 - Pb(NO_3)_2 - NH_4NO_3$	(134)	–
$KNO_3 - Pb_3O_4 - Pb(NO_3)_2$	(135)	–
$KNO_3 - TlNO_3 - KI$	(98)	–

The solid phase $KNO_3, 2HNO_3$, obtained in the binary system potassium nitrate-nitric acid, is very stable in the presence of excess nitric acid, and can serve as a source of very pure potassium nitrate or nitric acid.[136]

Aqueous Systems

Phase studies on aqueous systems containing potassium nitrate have been considerably extended, (cf. Mellor, II, 805, 813). In many instances the systems relate directly to the technical separation and purification of potassium nitrate from aqueous solutions.[137] Considerable detail is often available on the reciprocal aqueous systems known to be of technological interest.

TABLE IV. RECIPROCAL AQUEOUS SYSTEMS CONTAINING POTASSIUM NITRATE WHICH ARE OF TECHNOLOGICAL INTEREST

System	Reference
KNO_3 - NH_4Cl	(138)
KNO_3 - NaCl	(139)
KNO_3 - $CaCl_2$	(140)
KNO_3 - Na_2SO_4	(141) (141a) (142)
KNO_3 - Na_2SO_4 - NaCl	(141a) (143)
KNO_3 - $MgSO_4$	(144) (144a) (145)
KNO_3 - $(NH_4)_2SO_4$	(146)
KNO_3 - $Al(NO_3)_3$ - $Fe(NO_3)_3$	(147)
KNO_3 - $Al(NO_3)_3$	(148)
KNO_3 - $Fe(NO_3)_3$	(149)
KNO_3 - $Fe(NO_3)_3$ - HNO_3	(150)
KNO_3 - $AlCl_3$	(151)

Previous information on the potassium nitrate-nitric acid-water system, (Mellor, II, 820), has been supplemented.[152] The influence of nitric acid on the solubility of potassium nitrate is not due to complex formation. A eutectic of composition 2·90% of boric acid, 10·75% of potassium nitrate and 86·35% of water occurs in the potassium nitrate-boric acid-water system; no compound formation occurs, the potassium nitrate exerting a "salting in" effect on the boric acid.[153] Deviations from additivity of osmotic coefficients obtained from freezing point and conductivity data in the reciprocal salt pair, potassium nitrate-lithium chloride, are reported.[154] Knowledge of potassium nitrate-sodium nitrate-water system (Mellor, II, 805) has been extended by further measurements at 0°, 20°, 40° and 60°,[148] and at 90°[142] and above.[155] The addition of 0·15% by weight of agar-agar favours dendritic growth of the eutectic phases, but does not change the character of the crystallization process.[156]

Details of aqueous systems further to those reported in Mellor, II, are listed in Table V.

TABLE V. AQUEOUS SYSTEMS CONTAINING POTASSIUM NITRATE

System	Reference	Items of Special Note
KNO_3 - KNO_2	(157)	-
KNO_3 - KCl	(158)	-
KNO_3 - K_2SO_4	(159) (142) (142a)	Cryscopic constant for eutectic.[160]
KNO_3 - KCNS	(161)	-
KNO_3 - KBr	(161)	-
KNO_3 - $KClO_3$	(162)	-
KNO_3 - $KBrO_3$	(163)	-
KNO_3 - K vanadate	(164)	-
KNO_3 - K_2CrO_4	(165)	-
KNO_3 - K molybdate	(166)	-
KNO_3 - $Ca(NO_3)_2$	(167)	No double salt or mixed crystal observed.

(continued)

TABLE V. (continued)

System	Reference	Items of Special Note
KNO_3 – $Ba(NO_3)_2$	(168)	Evidence for double salt $K_2Ba(NO_3)_4$
KNO_3 – $Ba(NO_3)_2$ – $Pb(NO_3)_2$	(168)	Evidence for double salt $K_2Ba(NO_3)_4$
KNO_3 – $Mg(NO_3)_2$	(144) (144a)	-
KNO_3 – NH_4NO_3	(169)	Evidence for double salt $K_3(NH_4)(NO_3)_4$.[170]

Mixed crystals containing 19·3% potassium nitrate are formed between 85° and 95° from a saturated aqueous solution containing 80 parts of ammonium nitrate and 20 parts of potassium nitrate by weight. These mixed crystals of KNO_3 II and NH_4NO_3 III can also be prepared by heating the solids directly together.[170] The system potassium nitrate-potassium chloride-ammonium dihydrogen phosphate-water has been described over the temperature range −11·7° to 35°.[171] The polytherm for the reciprocal system $KNO_3 + (NH_4)H_2PO_4 \rightleftharpoons KH_2PO_4 + NH_4NO_3$ both as aqueous and melt systems is reported.[172] No double salt is observed in the potassium nitrate-sodium nitrate-aluminium nitrate-water system.[148] The system potassium nitrate-lead (II) nitrate-water,[168] investigated by determinations of magnetic susceptibility,[173] surface tension,[174] and compressibilities,[175] shows clearly the formation of three solid phases, $KNO_3,Pb(NO_3)_2$, $2KNO_3,Pb(NO_3)_2$, and $4KNO_3,Pb(NO_3)_2$. In the system potassium nitrate-uranyl nitrate-water, observed from −19·4° to 25°[176] and from 25° to 90°,[177] no double salts occur.

The eutectic point of the potassium nitrate-water system (−2·88°C.) serves as a useful cryoscopic point, and various molecular and ionic weights have been measured using this system.[178] The cryoscopic constant varies, with organic compounds values 16·4–16·6 apply, and with ionic compounds with an ion in common with potassium nitrate, 16·4–17·7.[179]

In view of the importance of crystallization from aqueous solution in the isolation of potassium nitrate, this aspect has received much attention. The velocity of crystal growth from a supersaturated solution increases with fall in temperature,[180] the values at 0° and 25° were measured and the kinetics analysed and interpreted in terms of dehydration of ions and adsorption.[181] The experimental data on the limiting supersaturation values can be related to the surface tension of the crystal.[182] The high supersaturation possible with potassium nitrate solutions is due to the fact that the salt may crystallize in different modifications. The supersaturation, $\rho = (c - c_0)/c_n$, where c_n = solubility and c = maximum solubility, was measured from 0° to 40°. Calculated values agree well with experimental values, $\rho = 0{\cdot}43$(calc.); 0·36(exp.).[183] The growth of rhombohedral crystals is promoted by the addition of 2-mole-% of lead (II) ions; thorium (IV) and bismuth (III) ions are also effective.[184] Large crystals can be obtained by the addition of wood or other vegetable extracts (e.g. pectin).[185] The tendency of potassium nitrate to crystallize in dendrites on slow evaporation is increased by the addition of gelatine or agar-agar.[186] The size of the crystals formed from a supersaturated solution at high rates of stirring, e.g. 180 r.p.m., is independent of the rate of cooling. The best results are obtained by adjusting the rate of stirring so that it is above that at which crystals agglomerate but below that at which very small crystals form.[187] Crystallization of a supersaturated solution is accelerated in the vicinity of an electrode charged with a frequency of 750–1000 Mc./sec.[188] The rate of solution of potassium nitrate, irrespective of the crystal form, is the same in 0·1 and 1·0N-hydrochloric and sulphuric acids and sodium hydroxide.[189] The ease of removal of thiocyanate, sulphate and nitrate ions from solid potassium nitrate, crystallized in acid (pH 2·5) and in alkaline (pH 10·6) solution, follows the Hofmeister series.[189] By the use of the ^{24}Na isotope, sodium nitrate has been shown to co-precipitate with potassium nitrate in an amount proportional to the concentration of the latter.[190] Crystals of potassium nitrate formed in solutions containing strontium nitrate labelled with a radioactive strontium isotope have the strontium largely in the periphery of the crystals; in the interior the amount is small and uniform and proportional to the amount of strontium in the solution.[191] The strontium removed on washing with saturated potassium nitrate solution varies exponentially with the number of washes.[192] Viscosity and temperature-dilation curves for supersaturated solutions show continuity between the saturated and supersaturated solution.[193] The vapour pressure of solutions saturated with potassium nitrate and with potassium nitrate and ammonium chloride, are shown in Table VI.[194]

TABLE VI. VAPOUR PRESSURES OF SATURATED SOLUTIONS OF POTASSIUM NITRATE ALONE OR MIXED WITH AMMONIUM CHLORIDE

°C	KNO_3 mm./Hg	$NH_4Cl + KNO_3$ mm./Hg
19·0	15·54	11·99
20·0	16·58	12·73
21·0	17·61	13·51
22·0	18·69	14·31
23·0	19·79	15·15
24·0	20·96	16·03
25·0	22·22	16·92
26·0	23·61	17·82
27·0	25·08	18·80
28·0	26·57	19·77
29·0	28·13	20·78
30·0	29·71	21·83

The relative humidity of air saturated by contact with saturated solutions of potassium nitrate from 0° to 50° is a continuous function of temperature.[195] The solubilities of potassium nitrate at temperatures in the range 100° - 450° are given in Table VII.[196]

TABLE VII.-SOLUBILITY OF POTASSIUM NITRATE AT VARIOUS TEMPERATURES

t°C.	%	t°C.	%
100	70·8	186	87·7
112	74·8	212	89·9
119	76·8	218	90·6
126	79·5	238	92·5
139	81·5	255	93·5
144	82·1	261	95·2
145	82·2	274	96·5
162	84·5	279	96·0
175	86·0	307	98·1

Careful measurement of the density of potassium nitrate solutions at 18° shows that there is a contraction on solution of 9·7 ml./mole at infinite dilution.[197] Various determinations of the refractive index of solutions of potassium nitrate have been made.[198] Table VIII gives the refractive index at three concentrations and two temperatures.[199]

An increase of pressure from 1 to 1000 bars at 25° on aqueous potassium nitrate containing respectively 8·16, 13·68, 20·22 and 26·53g. per 100g. water produces a decrease in volume per unit volume of 0·03663, 0·03482, 0·03283

Refs. p. 1940

TABLE VIII. REFRACTIVE INDEX OF AQUEOUS SOLUTIONS OF POTASSIUM NITRATE AT 20° AND 25°

	Concentration in mole/1000g. water		
	0·003989	0·019979	0·099969
Values of n_C at λ = 6563A.			
20°	1·331238	1·331407	1·332231
25°	1·330767	1·330928	1·331743
Values of n_D at λ = 5892A.			
20°	1·333099	1·333268	1·334090
25°	1·332578	1·332739	1·333555
Values of n_F at λ = 4861A.			
20°	1·337210	1·337381	1·338207
25°	1·336749	1·336913	1·337733

and 0·03093.[200]

The viscosity (0·1 to 0·0002M. at 25°) is given by the equation:-

$$\eta = 1 + 0{\cdot}0050\ c^{1/2} - 0{\cdot}0531c$$

where c is the molal concentration of potassium nitrate.[201] Over certain concentration ranges, the viscosity is less than that of water.[201,202]

The dielectric constant of aqueous potassium nitrate solutions decreases with increasing concentration. Activities for concentrated solutions calculated from this series of experiments agree only qualitatively with experimental values.[203] In water or glycerol the dielectric constant decreases linearly as the concentration increases.[204] A value of 151kg.-cal./mole is taken as the best value of the heat of hydration of the salt at infinite dilution.[205] By a study of the distribution of butyric acid between benzene, water and a molar solution of potassium nitrate, the degree of hydration per mole is found to be 4·6.[206] The heat of solution of $KNO_3,350H_2O$ at 21° (data corrected to this temperature)[207] is −8·580;[208] −8·37;[209] −8·409 and −8·417;[210] or −8·318kg.-cal.[211] The heat of solution at other dilutions and temperatures has been measured.[212] The heat of solution at the eutectic point is −6·5kg.-cal./mole;[213] the heat of solution at 40·5° is −5·57kg.-cal./mole.[214] Differences in the crystalline form of potassium nitrate are reflected in a difference of 0·15kg.-cal./mole in the heat of solution.[211] The liberation of 6kg.-cal. when 1 mole of potassium nitrate is added to 120 moles of nitric acid indicates the formation of a nitrate ion heavily solvated with nitric acid molecules.[215] The differential heats of dilution at various temperatures are reported.[216] The electrolytic conductance of solutions from 0·00003 to 0·1M. at 25° fits the Onsager equation at limiting values; Λ_0 = 144·92, at 0·0001M. Λ = 144·02, at 0·001M. Λ = 141·80, at 0·01M. Λ = 135·78, and at 0·1M. Λ = 120·36.[217] The data have been extended to 0°, 18°, and 100°[218] and 18° to 85°.[219] The electrolytic conductance at higher frequencies shows no significant difference from that at lower frequencies.[219] Evidence of osmotic and activity coefficients based on freezing point data,[220] conductivity,[221] and vapour pressure measurements,[222] suggest that dissociation in water is not complete. The densities and electrical conductivities at 25° of solutions containing 10, 25, 50, 75, and 90 mole-% of potassium nitrate, together with either potassium or sodium chloride to an overall molality of unity, indicate that only in the case of potassium chloride can the data be calculated from theory with precision.[223] The experimental data for these two systems have been extended to 0·05M. and 30°.[224] The value of Λ_0 at 25° for aqueous potassium nitrate in the presence of 10% and 20% of sucrose is 117·65 and 90·70, respectively.[225] The conductivity of potassium nitrate solution at concentrations of from 0·5 to 2·5M. in the presence of urea (19% and 35%), mannitol (3 – 9%), or sucrose (5 – 50%), is not dependent on the viscosity of the solution, the formulation of dissociable non-electrolyte-electrolyte complexes is postulated.[226] Potassium nitrate is commonly used as the supporting electrolyte in polarographic work and a number of papers have given data on the interfacial tension between mercury and potassium nitrate solutions.[227] The diffusion coefficient of potassium nitrate from conductimetric data has been applied to the calculation of activity coefficients.[228] In saturated solution the coefficient at 18·1° is $1{\cdot}171 \times 10^{-5}$cm.^{2}/sec.[229] At 25° in water at concentrations of 0·0284, 0·03033, 0·03742, 0·05010, 0·06045, 0·06995, 0·0800, 0·0910M., the differential diffusion coefficients are 1·815, 1·807, 1·786, 1·746, 1·672, 1·622, 1·586, $1{\cdot}547 \times 10^{-5}$cm.^{2}/sec., respectively.[230] The diffusion coefficient of potassium nitrate in nitric acid is independent of concentration in the range 0·001 to 0·1M.[231] The activity coefficients of potassium nitrate, measured by an isopiestic method, are 0·730, 0·656, 0·605, 0·540, 0·492, 0·439 at 0·1, 0·2, 0·3, 0·4, 0·5, 0·6M., respectively.[232] Under a potential drop of 10V./cm. in 1 hr. the electro-osmosis on paper electrophoresis was 0·029g. in 1·26cm.[233] The surface tension of aqueous solutions of potassium nitrate have the following values in dynes/cm. at 20° and 40° respectively:- 73·19, 70·21, at a concentration of 5·04% by weight; 73·87, 70·89 at 9·93%; 74·51, 71·52, at 14·22%; and in 10% aqueous acetone, 48·37, 44·99, at 4·97%; 47·73, 44·30, at 10·04%; and 47·11, 43·70, at 15·03%. Data are also available for 20% and 30% aqueous acetone[234] and for aqueous acetic acid.[235] The thermal expansion of aqueous potassium nitrate measured over 20° – 40°[236] and 20° – 70°[237] is reported; at 25°, but not at higher temperatures, the relation between the apparent expansibility and the square root of the concentration is linear.

The creeping of potassium nitrate solutions[238] can be stopped effectively by the addition of aluminium ions such that the Al^{3+} concentration exceeds the ratio $[Al^{3+}]/[KNO_3] = 5 \times 10^{-5}$. The effect is explained in terms of the selective adsorption of aluminium ions on the glass surface,[239] or in terms of surface tension.[240]

The diamagnetic susceptibility of potassium nitrate increases only slightly on passing from the solid to aqueous solution.[241] Specific heat measurements have been made on solutions of potassium nitrate at 21° at various concentrations up to the saturation point, and also at 41° and 86°, close to the saturation, point.[242] The specific heat of $KNO_3,25H_2O$ is 0·8335 at 20°, 0·83480 at 50°, and 0·83322 at 80°.[243]

Potassium nitrate added to gelatin solutions lowers the point at which the viscosity-temperature curve changes slope. Added to gelatin it has no effect on the coagulation by formalin, but influences the coagulation by chrome alum. This latter fact suggests that it may interact by blocking the end carboxyl groups.[244] The coagulation of rosin solution by the addition of potassium nitrate has been reported and discussed.[245] A solution of potassium nitrate sprayed into an aerosol produced mutual coagulation, the velocity varying directly with the amount and concentration of the solution.[246]

Solutions in Non-Aqueous and Mixed Solvents

The solubility of potassium nitrate in liquid ammonia per 100g. of solution is 9·59 ± 0·03g. at 0°, 10·56g. at 25° (ρ = 0·695 and 0·672g./ml.),[247] 9·52 at 0° and under a pressure of 3107mm.[248] 9·71 ± 0·05g. at 0·1° (ρ = 0·695g./ml.), 10·6 at 25°;[249] and per 100g. of liquid ammonia 10·4g. at 25°.[250] The molar heat of solution in liquid ammonia is –400g.-cal.[251]

Potassium nitrate is readily soluble in anhydrous hydrogen fluoride giving solutions of high conductance, e.g. Λ_{-15} for a 0·013 and 0·115M. solution are 622 and 482, respectively. The numerical values of molar conductance are roughly double those in water, probably due to the formation of K^+, $H_2NO_3^+$, and F^- ions in the solution.[252] The conductance of potassium nitrate in liquid hydrogen cyanide at 18° follows the expression $\Lambda_c = 353{\cdot}9 - 253\sqrt{c}$, $\Lambda_0 = 353{\cdot}9$.[253] The solubility at 0° is 0·050mole/l.[254]

The solubilities measured in water-hydrogen peroxide mixtures (0 - 100 mole%) at 0°, 15°, and 25°, show a discontinuity in the plot of mole fraction of hydrogen peroxide in the solvent against molality of salt.[255] At 25°, and 8·99 and 19·55 mole-% of hydrogen peroxide, the solubilities are 4·710 and 5·762 mole/1000g. of solution, respectively.[256]

The solubility in methyl alcohol-water mixtures at 25° is given in Table IX.[256]

TABLE IX. SOLUBILITY OF POTASSIUM NITRATE IN METHYL ALCOHOL-WATER MIXTURES

Weight %	Mole Fraction	*S* (mole/1000g. solution)
4·98	0·0286	3·046
9·45	0·0554	2·503
21·04	0·1303	1·522
40·30	0·2752	0·7130
59·94	0·4570	0·3125
70·05	0·5682	0·1898
78·96	0·6786	0·1123
89·45	0·8265	0·0607

The heat of solution in methyl alcohol at 0·0092M. at 20° is –4·19kg.-cal./mole. The heat of transference from methyl alcohol to water is +4·31kg.-cal./mole.[257] The data on the solubility of potassium nitrate in aqueous solutions of ethyl alcohol and *iso*propyl alcohol (Mellor, II, 817) have been extended, and solubility and density isotherms drawn for the potassium nitrate-ethyl alcohol-water system and the potassium nitrate-*iso*propyl alcohol-water system.[258, 259] The solubilities of potassium nitrate in methyl alcohol, ethyl alcohol, acetone, and ether, have been tabulated. Errors are often made in extraction analysis by ignoring this solubility.[260]

The molar conductance of potassium nitrate in dimethylformamide at 25°, at infinite dilution, is 88·1 and the dissociation constant (based on the Schedlovsky equation) is 0·043.[261] Potassium nitrate undergoes solvolysis in glacial acetic acid, the resulting solution being 'alkaline' with respect to acetic acid.[262] Data are available on the activity coefficient of potassium nitrate in glacial acetic acid, based on solubility measurements of the salt at 25° in the presence of ammonium chloride and ammonium nitrate.[263]

CHEMICAL REACTIONS

The action of heat on potassium nitrate, followed by differential thermal analysis, produces firstly a transition at 128°, corresponding to KNO_3 II → KNO_3 I, then melting at 332°, slight bubbling at about 628°, intensifying to vigorous bubbling at 642°. Slight nitrous fumes, corresponding to decomposition of the nitrite, are clearly visible at 805°.[264] Decomposition of potassium nitrate does not begin below 550°, but when the salt is mixed with sodium nitrate (45·5% of potassium nitrate), and in the presence of iron or aluminium as catalyst, decomposition occurs about 100° lower.[265] Spectroscopic examination of the vapour obtained by heating potassium nitrate in a sealed quartz tube showed the presence of nitric oxide at temperatures above 550°. The molecules of potassium nitrate are not ionised in the vapour state.[266] The temperature of dissociation under 1 atm. of carbon dioxide is 532·7°.[267] A patent refers to the reduction of alkali nitrate by hydrogen at about 400° to give nitrite.[268] Reaction with hydrogen in a silent electric discharge leads to potassium nitrite, potassium hydroxide, and ammonia.[269] Potassium nitrate can be completely reduced in cold aqueous solution by metallic iron in the absence of oxygen.[270] In liquid ammonia solution, potassamide reacts with potassium nitrate, in the presence of various metal oxides acting as catalysts, according to the equation:-

$$3KNH_2 + 3KNO_3 \rightarrow 3KOH + N_2 + NH_3 + 3KNO_2$$

Ferric oxide, cobaltic oxide, and nickelous oxide are good catalysts for this reaction.[271] Solutions of potassium in liquid ammonia can reduce potassium nitrate to potassium nitrite.[272]

Seven papers describe the effect of light on aqueous solutions of potassium nitrate to give potassium nitrite. The reaction is accelerated by the addition of alkali.[273] The photolysis of aqueous potassium nitrate has been used to calibrate the apparatus used for the study of the photochemical decomposition of solid potassium nitrate by light from a high pressure mercury arc. The approximate quantum yield is 0·098.[274] The quantum efficiency at 2540 A. increases with pH, up to 0·25 at pH 9·9, thereafter remaining constant.[275] Decomposition is initially only in the surface layers of the crystal.[276]

The effect of *X*-rays (0·24A.) on potassium nitrate solutions shows that $5{\cdot}58 \times 10^{11}$ molecules react per Roentgen unit, or 0·2 molecules per ion pair. The energy involved is $1{\cdot}31 \times 10^7$ g.-cal./mole.[277] The radiolysis of aqueous potassium nitrate is due to the formation of hydrogen or hydroxyl radicals in the solution.[278] In 0·01 to 1·0M. solutions, an efficiency of 2 mole/100e.V. is obtained using ^{60}Co as the source. The addition of glucose accelerates the reduction.[279] Solutions of potassium nitrate can be reduced anodically in glow discharge electrolysis.[280]

Reaction of potassium nitrate with concentrated aqueous hydrogen fluoride gives $K_2N_2O_5F_2$.[281] The action of elemental fluorine on solid potassium nitrate yields the gaseous product NO_3F (see Mellor, II, Suppl. I, 59).[282] The action of sulphur trioxide on solid potassium nitrate at 20° – 30° produces a colourless, clear liquid, which on removal of excess sulphur trioxide gives white crystals consisting of $K_2S_3O_{10}$ and $N_2O_5,4SO_3$.[283] Complete conversion of potassium nitrate to potassium borate occurs at 500° on heating a mixture containing 8 parts of boric acid and 1 part of potassium nitrate for 10 min.[284]

A large number of papers report the 'salting in' or 'salting out' effect of potassium nitrate on various organic compounds soluble in water.[285] The solubilities in potassium nitrate solution of the oxalates of calcium, strontium, barium, cadmium, copper, and lead increase as the concentration of potassium nitrate is increased. The lower the solubility of the oxalates in water, the lower it is in potassium nitrate.[286] The 'salting out' coefficients, $(\log_{10}s_0/s)/c$, (where s_0 = cc. at N.T.P. in water, s = cc. at a total pressure of 1 atm. in solution, and c = concentration in moles, all in 1000g. of water) are 0·093 for krypton, and 0·120 for sulphur hexafluoride.[287]

APPLICATIONS

Potassium nitrate has found application in qualitative analysis as an oxidising agent. A method of solution involving initial fusion with potassium hydroxide, potassium carbonate and potassium nitrate, followed by extraction with water, divides the elements clearly into two groups, those yielding insoluble oxides and hydroxides, and those going directly into solution.[288] Mixtures of lithium hydroxide and potassium nitrate, and of potassium hydroxide and potassium nitrate, have been used successfully to replace ammonium polysulphide in the division of the sulphide precipitate into two portions.[289]

Little further has been added to existing knowledge (Mellor, II, 825) on the use of potassium nitrate in "gunpowder" and related compositions. The setting of potassium nitrate on storage can be prevented by the addition of 0·05-0·1% of either sodium 1,4-diamino-2-anthraquinonesulphonate or 1,4,5,8-tetra-aminoanthraquinonedisulphonate.[290] The initiation reaction of gunpowder originates in hot spots formed by adiabatic compression or by the friction of grit particles, a temperature of 130° which is sufficient to melt the sulphur being reached. The occurrence of a liquid phase is important, as it reacts with the oxy-hydrocarbons present in the charcoal. This reaction develops until the oxidation of the charcoal by potassium nitrate commences. Propagation from grain to grain is probably caused by emission of a hot spray of potassium salt droplets.[291] Stearic acid acts as an inhibitor in the burning of gunpowder, but sulphur counteracts this inhibiting effect. With other fatty acids the effect is less marked, but increases with chain length. This is a surface effect, the acid preventing reaction between the charcoal and potassium nitrate.[292] A study of the reaction of mixtures of potassium nitrate and charcoal has shown that oxygen and nitrous oxide are absent from the gases produced, and potassium cyanide and potassium cyanate from the residues. At about 250° (below the m.p. of potassium nitrate) the main reaction is:-

$$2KNO_3 + C \rightarrow 2KNO_2 + CO_2$$

further reaction then occurs thus:-[293]

$$4KNO_2 + 3C \rightarrow 2K_2CO_3 + CO_2 + 2N_2.$$

Heterogenous pre-ignition reactions occur with combustible substances and potassium nitrate, e.g. with 80% potassium nitrate the minimum temperature of initiation with carbon black is 415°, with the evolution of 19·5kg.-cal., with paraffin wax, 590°, with starch, 391°, and with asphalt, 485°.[294] Potassium nitrate continues to find new applications in explosives. For example, potassium nitrate added to ammonite explosives reduces the formation of nitrogen oxides and of carbon monoxide.[295] An explosive powder with a high temperature of deflagration is described consisting of an oxidant, such as potassium nitrate, along with a combustible substance such as nitroguanidine or hexanitrodiphenylamine. An example of a mixture consisting of 50% of nitroguanidine and 44% of potassium nitrate is quoted.[296] A mixture comprising 60 parts of potassium nitrate and 40 parts of calcium silicide acts an excellent primer for various reactions.[297] A fertiliser mixture consisting of 34·6% of ammonium chloride and 65·4% of potassium nitrate is practically non-explosive.[298]

Dilute aqueous potassium nitrate solution in the presence of formaldehyde or methyl alcohol under ultra-violet light, gives formhydroxamic acid, HC(=NOH)OH. This is also the product of irradiation of a solution of potassium nitrate containing carbon dioxide.[299] Mixed amino acids have been identified in the products of the reactions of aqueous solutions containing potassium nitrate, and paraformaldehyde in the presence of ferric chloride as catalyst, the reaction occurring only under the influence of light. Potassium nitrate is reduced by various species of *Euglenidae*.[301] The addition of potassium nitrate to cheese results often in a patchy coloration due to the reduction to nitrite by nitrate-reducing bacteria.[302] Potassium nitrate used in the curing of meats is reduced to potassium nitrite by micro-organisms.[303] The effect of potassium nitrate on the redox potential of cheese and its relation to the ripening of cheese is recorded.[304] Various suggestions have been made to incorporate potassium nitrate in mixed fertilisers or to use it directly as a fertiliser.

Though its cost of manufacture is such that potassium nitrate probably can never compete with other sources of nitrogen, various papers concerning its use in mixed fertilisers continue to appear.[305] In special cases, such as in horticulture or in concentrated fertilisers, potassium nitrate may find a useful place.[306] Fertiliser potassium nitrate has been reported as free from manganese.[307] Phosphate suffers increased adsorption by soil and thereby a lower mobility in the presence of potassium nitrate in acid solution.[308] Potassium nitrate may lead to excessively alkaline soils if applied in large amounts.[309] The effect of potassium nitrate on the colloidal properties of the soil have been described.[310] The use of 2:4-dinitrophenoxyacetic acid as an insecticide increases the concentration of potassium nitrate in leaves. The amount may reach levels toxic to animals.[312]

Molten potassium nitrate is used in the heat treatment of steel, producing less deformation and increased surface hardness and strength.[313] In the treatment of light metals, bath temperatures of the order of 500° are maintained.[314] A mixture of potassium nitrate (1 part) and ferrosoferric oxide (8 parts) is a suitable composition for starting an arc in arc-welding procedures.[315] Molten potassium nitrate and mixtures with sodium nitrate and sodium nitrite have been studied as high temperature heat transfer materials.[316] Potassium nitrate added to boiler water suppresses corrosion.[317] The setting of plaster of Paris is accelerated by the addition of potassium nitrate.[318] The use of a 1:1 mixture of molten sodium nitrate and potassium nitrate, as a substitute for Babbitt metal in securing good fitting between emery stones and rolls has been suggested.[319] Potassium nitrate and kaolin is a good lubricant at high temperatures, as also are calcium nitrate, potassium nitrate and kaolin mixtures.[320]

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SECTION LVIII

POTASSIUM PHOSPHATES

By J. S. RAITT

In recent years, much work has been done in the study of phosphorus compounds generally by J. R. Van Wazer and his co-workers. Much of this work concerns the orthophosphates or condensed phosphates of potassium, and a great deal of valuable and well documented information about these substances is to be found in Van Wazer's recent book on the chemistry of phosphorus and its compounds.[1] Information bearing on potassium phosphates is provided also by the work of Thilo, who has made comprehensive studies of condensed phosphates and the analytical methods applicable to them.[2] The preparation and uses of some condensed phosphates of potassium are discussed by Bigeon in a review dealing with alkali metal phosphates,[3] and the phase equilibria in aqueous solution of the various orthophosphates of potassium are fully described by Wendrow and Kobe in a recent review concerned with alkali metal orthophosphates.[4]

TERTIARY POTASSIUM ORTHOPHOSPHATE

Bykov[5] has described a method for the manufacture of tertiary potassium orthophosphate by first calcining at 600°C. for 20 min. minerals such as vivianite, kertschenite, beraunite, bosphorite or synthetic precipitated iron phosphates. After treatment of the product with excess of potassium hydroxide, ferric hydroxide is filtered off and the solution cooled to −5°C. when a hydrate of tertiary potassium orthophosphate crystallises out. Concentration of the remaining solutions can yield more of the hydrated tertiary salt; alternatively, potassium dihydrogen phosphate may be obtained by the addition of orthophosphoric acid. The reaction between phosphoric acid and potassium chloride has also been used to prepare tertiary potassium phosphate by a process which employs also sufficient sulphuric acid to drive off the chloride as hydrogen chloride.[6] At high temperatures, tertiary potassium phosphate can be made by heating chromium ore, crude phosphate, coke and silica in an electric furnace.[7]

An interesting process exists for the separation of tripotassium phosphate and potassium aluminate present in the same solution.[8] When gaseous ammonia is passed through the solution, two layers are formed, the lower containing most of the phosphate and the upper containing the aluminate. More complete separation may be achieved after the initial separation of the layers by diluting them and passing ammonia again.

A solubility diagram given by Ravich for tertiary potassium phosphate in water appears in Fig. 1 and shows the existence of a trihydrate, a heptahydrate and a nonahydrate.[9] The nonahydrate has a stability range from −24°C. to −15°C., while the heptahydrate is stable above −15°C. and has a solubility maximum at 45·6°C. The trihydrate is stable above 45·4°C. Numerical values given by Ravich for the polytherm of K_3PO_4 appear in Table I. Jänecke has also studied this system, and reports the existence of an octahydrate with m.p. 45°C.[10] The solubility values which he gives

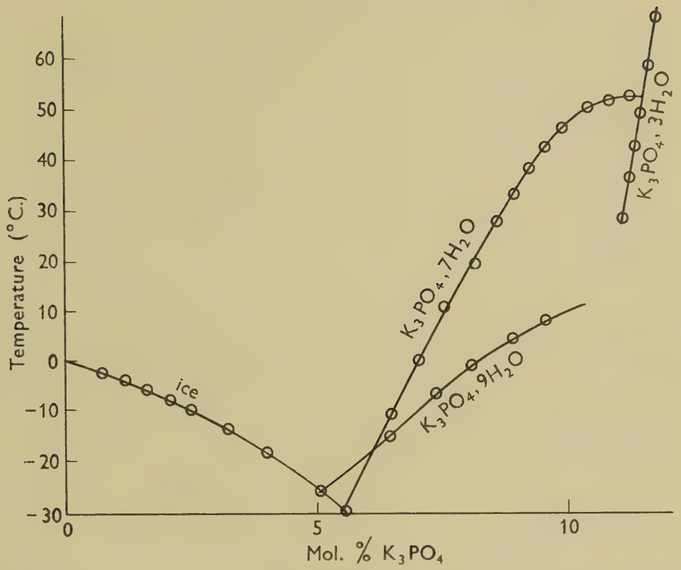

FIG. 1.- POLYTHERM OF THE SOLUBILITY OF K_3PO_4 IN WATER

TABLE I.- POLYTHERM OF THE SOLUBILITY OF K_3PO_4 IN WATER

Wt.-%	Mol. %	Temp. in °C.	Solid phase	Remarks
4·54	0·40	−1·18	Ice	
9·75	0·91	−2·60	Ice	
15·43	1·52	−4·6	Ice	
21·74	2·30	−7·7	Ice	
27·34	3·09	−12·0	Ice	
31·53	3·76	−15·8	Ice	
35·12	4·39	−20·0	Ice	
38·33	5·00	−24·0	Ice + $K_3PO_4,9H_2O$	
40·25	5·40	−28·2	Ice + $K_3PO_4,7H_2O$	Metastable eutectic
42·92	6·00	−8·8	$K_3PO_4,7H_2O$	
44·26	6·31	0	$K_3PO_4,7H_2O$	
46·83	6·95	+10·0	$K_3PO_4,7H_2O$	
49·62	7·71	+20·0	$K_3PO_4,7H_2O$	
51·42	8·23	+25·0	$K_3PO_4,7H_2O$	
53·08	8·75	+30·0	$K_3PO_4,7H_2O$	
55·43	9·54	+35·0	$K_3PO_4,7H_2O$	
57·51	10·30	+40·0	$K_3PO_4,7H_2O$	
59·46	11·06	+42·6	$K_3PO_4,7H_2O$	
60·84	11·64	+44·5	$K_3PO_4,7H_2O$	
61·94	12·13	+45·4	$K_3PO_4,7H_2O$	
62·51	12·39	+45·6	$K_3PO_4,7H_2O$	
63·12	12·68	+45·6	$K_3PO_4,7H_2O$	
—	—	+45·4	$K_3PO_4,7H_2O$ + $K_3PO_4,3H_2O$	
63·17	12·70	+25·0	$K_3PO_4,3H_2O$	Metastable
63·19	12·71	+30·0	$K_3PO_4,3H_2O$	Metastable
63·33	12·77	+35·0	$K_3PO_4,3H_2O$	Metastable
63·41	12·81	+40·0	$K_3PO_4,3H_2O$	Metastable

continued on following page

TABLE I.- CONTINUED

Wt.-%	Mol. %	Temp. in °C.	Solid phase	Remarks
63·56	12·89	+45·0	$K_3PO_4,3H_2O$	Metastable
63·80	13·00	+50·0	$K_3PO_4,3H_2O$	
64·08	13·14	+60·0	$K_3PO_4,3H_2O$	
43·85	6·21	−7·7	$K_3PO_4,9H_2O$	Metastable
47·62	7·16	0	$K_3PO_4,9H_2O$	Metastable
49·80	7·70	+5·0	$K_3PO_4,9H_2O$	Metastable
52·23	8·49	+8·8	$K_3PO_4,9H_2O$	Metastable
57·72	10·00	+12·3	$K_3PO_4,9H_2O$	Metastable

for this salt are very near to those of Ravich for $K_3PO_4,7H_2O$, however, and it may be that the salt believed by Jänecke to be the octahydrate was the heptahydrate found in Ravich's later work. The heptahydrate can be crystallised from its saturated solutions by cooling them, but solutions of the trihydrate have to be evaporated to isolate this salt, owing to the very small temperature coefficient of its solubility.

The coefficient of thermal expansion of tertiary potassium phosphate has been determined at 19°C., −78°C. and −195°C. and the relations extrapolated to absolute zero.[11] Over the range 17°C. to −78°C., $a \times 10^5$ is given the value of 12. At lower temperatures, values are 8 over the range −78°C. to −195°C., and 4 from −195°C. to −273°C.

The heats of solution and dilution of tertiary potassium phosphate have been determined:[12] over the concentration range 0 to 4 moles per 100 moles of water, the integral heat of solution, Lc (g.-cal./mole), is given by the relation:- $Lc = 9538 + 823{\cdot}3C + 188{\cdot}9C^2 + 13{\cdot}01C^3$ where the concentration, C, is expressed as moles of salt per 100 moles of water.

Three, and possibly all four, of the oxygen atoms in tertiary potassium phosphate may take part in exchange with ^{18}O when the salt is treated at room temperature with water enriched with this isotope.[13]

The Raman spectrum of tertiary potassium phosphate is reported by Venkateswaran and by Simon and Feher.[14,15]

The dielectric constant of tertiary potassium phosphate is reported to be 7·75,[16] and to show only small variations with temperature.[17]

The reactions taking place when ammonia is passed into solutions of tertiary potassium phosphate have been studied by Jänecke, who reports that two layers are formed in the solution.[18] Separation of hydrated tertiary potassium phosphate then occurs, followed by the disappearance of the heavier layer. Dilution with water, or heating, causes complete miscibility.

Solutions of magnesium chloride and tertiary potassium phosphate precipitate $MgKPO_4,nH_2O$, which changes in composition to $Mg(OH)_2,2MgHPO_4,xH_2O$ with increasing magnesium concentration.[19] To obtain complete precipitation of magnesium as the normal phosphate, it is necessary to use up to double the theoretical amount of tertiary potassium phosphate.

Tertiary potassium phosphate shows pronounced catalytic activity in the atmospheric oxidation of carbon black, but not when the oxidation is effected by potassium chlorate.[20,21] When used as a promoter with an activated carbon catalyst in naphtha reforming, tertiary potassium phosphate retards cracking and assists dehydrogenation.[22]

In the treatment of feed-water to boilers operating high pressure turbines, tertiary potassium phosphate has been found to be very successful in reducing the formation of salt deposits in the turbines.[23] Another application is the selective removal of hydrogen sulphide from gas mixtures.[24,25] The salt has also been used to increase the fluidity of china clay suspensions.[26] It is claimed to have good properties as a fire-retardant.[27]

SECONDARY POTASSIUM ORTHOPHOSPHATE

Secondary potassium phosphate, K_2HPO_4, free from the tertiary salt, can be made by passing ammonia into a solution of potassium dihydrogen phosphate in sufficient quantity to form triammonium phosphate. The trihydrate of this salt may be crystallised out and secondary potassium phosphate recovered from the remaining solution.[28] Potassium ammonium hydrogen phosphate can be made by treating a phosphorite with sulphuric acid and then with solutions of potassium and ammonium sulphates.[29]

Secondary potassium phosphate forms a trihydrate which is stable between 14·3°C. and 48·3°C. and a hexahydrate stable from −13·5°C. to 14·3°C.[9,30] By the evaporation of a solution of the salt in hydrogen peroxide, a compound of the composition $K_2HPO_4,2{\cdot}5H_2O_2$ may be formed.[31]

The heats of solution and of dilution of secondary potassium phosphate have been determined by Khomyakov *et al.*[12] Over the concentration range 0 to 10 moles in 100 moles of water, the integral heat of solution, Lc (g.-cal./mole), is given by the relation:- $Lc = 4495 + 511{\cdot}72C - 63{\cdot}85C^2 + 2{\cdot}39C^3$ where the concentration, C, is expressed as moles of salt per 100 moles of water. The heat of dilution is given by the expression:- $dL/dc = 25{\cdot}50 - 15{\cdot}91C + 1{\cdot}378C^2$ for values of C ranging from 10 to 18.

The Raman spectrum of secondary potassium phosphate is reported by Venkateswaran[14] and by Simon and Feher.[15] Infra-red absorption data given by Corbridge and Lowe for the 650–4000 cm.$^{-1}$ region[32] are shown in Table II.

TABLE II.- THE POSITIONS AND INTENSITIES OF INFRA-RED ABSORPTION BANDS OF POTASSIUM PHOSPHATES

Substance	Absorption (wave no., cm.$^{-1}$)	
KH_2PO_4	1285 *s*, *vb*	
	1085 *s*, *vb*	
	890 *s*, *vb*	
K_2HPO_4	2900 *m*	996 *s*
	2550 *w*	983 *s*
	1650 *w*, *b*	952 *m*
	1328 *w*	847 *s*, *b*
	1110 *vs*, *b*	800 *w*
$K_4P_2O_7$	1110 *vs*	980 *w*
	1080 *s*, *sh*	930 *m*
	1050 *s*, *sh*	890 *vs*, *b*
	1025 *s*	720 *m*
$K_5P_3O_{10}$	1208 *s*	874 *vs*, *vb*
	1156 *s*	726 *m*
	1130 *vs*, *b*	683 *m*
	1090 *s*	
$(KPO_3)_n$	1300 *s*	1015 *w*, *b*
	1266 *vs*	851 *vs*, *b*
	1150 *s*	760 *m*
	1100 *s*, *b*	677 *s*

The equation below has been given for the refractive index of solutions of secondary potassium phosphate:-[33] $n_D^{25} = 1{\cdot}360C + n'^{25}_D$ where C = the concentration of secondary potassium phosphate in g. for 100 ml. of solution and n'^{25}_D = the refractive index of water at 25°C. for sodium light of $\lambda = 589\,m\mu$.

The dielectric constant of secondary potassium phosphate has been found to be 9·05, and at low temperatures this decreases regularly with temperature.[16,34] Only slight variation of the dielectric constant with temperature has been found at 9500 Mc.[17] The electrolytic oxidation of secondary potassium phosphate gives rise to the perphosphate and the monoperphosphate, but conditions may be chosen to give an 80% yield of perphosphate.[35,36] Phosphate and perphosphate may be separated by means of magnesia mixture, which does not precipitate perphosphate.[36]

The solubility curve of secondary potassium phosphate has been determined[9,37] and is shown in Fig. 2. Numerical values for the polytherm appear in Table III.

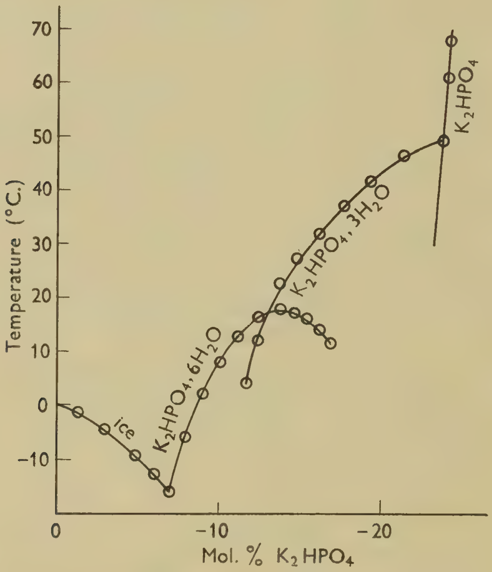

FIG. 2.- POLYTHERM OF SOLUBILITY OF K_2HPO_4 IN WATER

TABLE III.- POLYTHERM OF THE SOLUBILITY OF K_2HPO_4 IN WATER

Wt.-%	Mol. %	Temp. in °C.	Solid phase	Remarks
16·78	2·04	−4·2	Ice	
23·60	3·09	−6·4	Ice	
29·61	4·17	−9·0	Ice	
34·10	5·07	−11·7	Ice	
36·78	5·67	−13·5	Ice + $K_2HPO_4,6H_2O$	
46·11	8·12	0	$K_2HPO_4,6H_2O$	
50·12	9·40	+4·95	$K_2HPO_4,6H_2O$	
54·43	10·99	+9·7	$K_2HPO_4,6H_2O$	
57·89	12·44	+13·15	$K_2HPO_4,6H_2O$	
—	—	+14·3	$K_2HPO_4,6H_2O$ + $K_2HPO_4,3H_2O$	
60·82	13·82	+14·6	$K_2HPO_4,6H_2O$	Metastable curve of the solubility of $K_2HPO_4,6H_2O$
61·73	14·29	+14·85	$K_2HPO_4,6H_2O$	
62·96	14·94	+14·7	$K_2HPO_4,6H_2O$	
65·95	16·68	+12·8	$K_2HPO_4,6H_2O$	
69·09	18·75	+8·2	$K_2HPO_4,6H_2O$	
57·05	12·01	0	$K_2HPO_4,3H_2O$	Metastable curve of the solubility of $K_2HPO_4,3H_2O$
59·08	12·96	+10·0	$K_2HPO_4,3H_2O$	
60·16	13·49	+15·0	$K_2HPO_4,3H_2O$	
61·52	14·16	+20·0	$K_2HPO_4,3H_2O$	

continued on following page

TABLE III.- CONTINUED

Wt.-%	Mol. %	Temp. in °C.	Solid phase	Remarks
62·74	14·83	+25·0	$K_2HPO_4,3H_2O$	
64·13	15·60	+30·0	$K_2HPO_4,3H_2O$	
65·68	16·51	+35·0	$K_2HPO_4,3H_2O$	
67·54	17·68	+39·5	$K_2HPO_4,3H_2O$	
69·83	19·29	+44·0	$K_2HPO_4,3H_2O$	
71·26	20·42	+46·0	$K_2HPO_4,3H_2O$	
72·64	21·55	+51·0	K_2HPO_4	
72·50	21·38	+56·0	K_2HPO_4	
72·79	21·66	+63·0	K_2HPO_4	

It may be noted that although $K_2HPO_4,3H_2O$, and $K_2HPO_4,6H_2O$ can be crystallised by cooling their saturated solutions, the anhydrous salt itself, K_2HPO_4, cannot be prepared in this way because of the very small value of the temperature coefficient of its solubility. The mutual solubility of secondary potassium phosphate and diammonium phosphate in water has also been studied,[38] and the results are shown in Table IV.

TABLE IV.- THE MUTUAL SOLUBILITY OF K_2HPO_4 AND $(NH_4)_2HPO_4$ IN WATER AT 0°C.

Composition of liquid phase Wt.-%			Composition of residue Wt. %			Solid phase
$(NH_4)_2HPO_4$	K_2HPO_4	H_2O	$(NH_4)_2HPO_4$	K_2HPO_4	H_2O	
36·24	–	63·76	–	–	–	$(NH_4)_2HPO_4$
31·93	7·94	60·13	–	–	–	$(NH_4)_2HPO_4$
28·60	15·66	55·74	71·98	5·60	22·42	$(NH_4)_2HPO_4$
27·36	17·82	54·82	–	–	–	$(NH_4)_2HPO_4$
21·39	29·34	49·27	71·35	10·43	19·22	$(NH_4)_2HPO_4$
17·86	38·35	43·79	75·37	11·13	13·50	$(NH_4)_2HPO_4$
15·01	43·74	41·25	–	–	–	$(NH_4)_2HPO_4$
14·87	48·90	36·23	–	–	–	$(NH_4)_2HPO_4 + K_2HPO_4,6H_2O$
14·66	48·58	36·76	7·23	55·75	37·02	$K_2HPO_4,6H_2O$
9·35	48·52	42·12	6·24	53·67	40·69	$K_2HPO_4,6H_2O$
6·22	48·14	45·64	1·91	57·64	41·45	$K_2HPO_4,6H_2O$
4·59	47·64	47·77	1·15	58·61	40·24	$K_2HPO_4,6H_2O$
–	45·72	54·28	–	–	–	$K_2HPO_4,6H_2O$

Various inorganic salts, including the halides and nitrates of sodium and of potassium, have been reported to lower the *p*H of solutions of secondary potassium phosphate, and to cause errors of the order of 1–2% in *p*H titrations of phosphoric acid when present in concentrations comparable with that of the phosphate.[39]

The thermal dehydration of secondary potassium phosphate starts near 280°C., and a product consisting of about 50% of potassium pyrophosphate may be obtained by heating the salt at 325°C.[40] Almost complete conversion to the pyrophosphate occurs on heating at 400°C.[40] Normal potassium triphosphate is formed during the heating of mixtures of primary and secondary potassium phosphates in molar ratios of 1:2.[40] When mixtures of primary and secondary potassium phosphates are heated to about 250°C., a pyrophosphate of the composition $K_3HP_2O_7$ can be formed.[40] On further heating to a higher temperature, this substance may form potassium metaphosphate and normal potassium triphosphate, or, if excess of secondary potassium phosphate is present, may react with this to form only normal potassium triphosphate.[40] The heating of equimolecular mixtures of secondary potassium phosphate and potassium bisulphate to 200°C. results in the formation of potassium sulphate and dehydration products of primary potassium phosphate.[41]

Stepwise dehydration on heating has been reported for substances described as $K_2HPO_4,KH_2PO_4,3H_2O$, $K_2HPO_4,KH_2PO_4,2H_2O$, $3K_2HPO_4,KH_2PO_4,2H_2O$ and $2K_2HPO_4,KH_2PO_4,H_2O$.[42] The thermal dehydration of arsenatophosphates such as $K_2H(P,As)O_4$ forms only diarsenatophosphates, $K_4(P,As)_2O_7$, when the atomic ratio of arsenic to phosphorus in the initial mixed crystals is near unity. When twice, or more than twice, as many arsenic atoms as phosphorus atoms are present, the intermediate formation of triarsenatophosphates such as $K_3H_2(As, P)_3O_{10}$ can occur.[43]

The solubility of trisilver orthophosphate is reported to be greatly increased in solutions of secondary potassium phosphate.[44]

Secondary potassium phosphate has little application as an agricultural fertiliser, but it has been shown that the potassium and phosphorus in it are available to plants.[45] The fixation of phosphorus from solutions of the salt by iron and aluminium silicates has been found to increase linearly with the amount of silicate used and to be greater with the aluminium compounds.[46]

Studies of the effect of various inorganic salts on the interfacial tension at the water–mercury boundary showed that one of the highest values occurred with solutions of secondary potassium phosphate.[47]

PRIMARY POTASSIUM ORTHOPHOSPHATE

Large, prismatic, piezoelectric crystals of primary potassium phosphate may be grown from seed crystals suspended in a saturated solution to which potassium carbonate and potassium borate have been added.[48,49] The formation of large, pure, structurally uniform crystals is favoured by the presence of excess of potassium, and by maintaining the pH of the solution near 5, with the borate. Accurate temperature control, with slow cooling at the rate of 0·1°C. per day for 6½ months, gives the best crystals, but more rapid growth is possible in a special apparatus.[48,50]

Solutions of impure primary potassium phosphate frequently form deposits on standing owing to the separation of colloidal compounds of iron and aluminium. Purification can be achieved if a 0·2 M. solution of the salt is allowed to stand in a sealed flask at 75–85°C. for 24 hr. After filtering this solution, the pure salt may be recovered by recrystallisation of the residue obtained on evaporation, or by precipitating the salt from the cold, saturated solution by adding an equal volume of 95% ethyl alcohol.[51]

Primary potassium phosphate is normally manufactured by treating potassium carbonate, or bicarbonate, with phosphoric acid.[52] Crude phosphoric acid made from phosphatic material containing iron and aluminium can be used to yield a non-hygroscopic product by this reaction.[53] The utilisation of the potassium in minerals such as wyomingite has been studied for the manufacture of primary potassium phosphate.[54] When finely ground, 100 lb. of wyomingite readily yield 8 lb. of soluble K_2O by ion exchange with sodium salts, under pressure at 200°C.[55,56] If the ion exchange is effected with sodium carbonate, the resulting solution need only be neutralised with phosphoric acid to produce a solution of primary potassium phosphate. If sodium chloride is used for the ion exchange step, primary potassium phosphate may be made by treating the solution of potassium chloride with phosphoric and sulphuric acids at higher temperatures.[55] Primary potassium phosphate can be made by causing potassium chloride to react with phosphoric acid. When these two substances are heated together in equimolecular proportions at atmospheric pressure, a temperature high enough to cause condensation of the phosphate to metaphosphate is needed to remove all the chloride by volatilisation as hydrogen chloride. If excess of phosphoric acid is used, however, complete elimination of the chloride can be achieved at much lower temperatures.[57] Methods for the manufacture of primary potassium phosphate in this way have been described and these employ about a two-fold excess of phosphoric acid.[58-61] Primary potassium phosphate is obtained by crystallisation from these solutions when they are cooled and diluted with water to decompose the compound, KH_2PO_4,H_3PO_4. This technique has been developed into a cyclic process, in which equimolecular amounts of potassium chloride and phosphoric acid are introduced into a solution saturated with primary potassium phosphate and also with the compound KH_2PO_4,H_3PO_4. This solution is sufficiently strongly acid to permit the volatilisation of all the chloride as hydrogen chloride by boiling. Additions of water are made during the heating and primary potassium phosphate is obtained after the reaction has been completed by cooling the solution. This solution is then used again for the first stage of the process.[62-69] In this process, the elimination of chloride takes place more readily at higher reaction temperatures. If a temperature of about 300°C. is used, a mixture of condensed phosphates is formed. These may be hydrolysed to orthophosphate by subsequently heating the diluted reaction solution at about 250°C., with additional phosphoric acid if necessary.[70,71] Potassium chloride has also been used to prepare primary potassium phosphate from primary ammonium phosphate by a similar reaction. When equimolecular proportions of ammonium phosphate and potassium chloride are heated together at 250°C. in a current of steam for 6 hr., a 79% yield of primary potassium phosphate can be obtained.[72] Higher yields of mixtures of ammonium and potassium phosphates suitable for fertiliser purposes can be obtained in this way.[73] Phosphates of potassium and ammonium may be separated from solutions containing both by passing sufficient ammonia to form the secondary or tertiary ammonium phosphates which may be crystallised out after concentrating and cooling the solutions. Phosphoric acid is then added to form a solution of the primary salts from which primary potassium phosphate can be crystallised.[74-76] The preparation of primary potassium phosphate from potassium chloride without driving off the hydrogen chloride by heating has recently been described.[77] In this method, the hydrogen chloride is removed by extraction with suitable organic solvents which are recovered by distillation. The method is widely applicable to many preparations. Primary potassium phosphate can be made by various methods from phosphate rock and other natural phosphates. These methods include the formation of the potassium salt by treating with potassium chloride a solution of primary sodium phosphate made from the natural phosphate by attack with a mineral acid, followed by neutralisation with sodium carbonate.[78] Crude phosphates can also be treated with a solution containing potassium bisulphate, potassium sulphate, hydrochloric acid and sulphur dioxide. Calcium sulphate is separated by filtration and primary potassium phosphate is recovered by crystallisation when the solution is cooled.[79] The salt has also been made in a process involving the high-temperature treatment of iron phosphates.[5]

Primary potassium phosphate crystallises in the tetragonal scalenohedral class.[80] The tetragonal unit cell of the lattice measures 7·42 A. along the base-edge (*a*), is 6·97 A. in height and has a ratio *c*/*a* of 0·939.[80] The space group is $F\bar{4}d2$ and the unit cell contains four molecules.[81-83] *X*-Ray and neutron diffraction studies have shown that the PO_4 tetrahedra are very nearly regular, and that they become almost exactly regular at low temperatures.[82-85] The substance contains sufficient hydrogen atoms to allow H-bonds to be formed between all the oxygen atoms in the crystal, and the PO_4 tetrahedra are linked together in this way to form a three-dimensional structure. At temperatures above the Curie point, the hydrogen atom in the O–H–O hydrogen bond has been shown to be elongated along the axis of the bond.[84] The hydrogen atoms are located almost midway between the oxygen atoms of the bond, but may occupy positions about 0·15 A. nearer to one oxygen atom than to the other.[84,86] The O–H–O bonds are inclined at not more than 0·5° to the *xy*-plane.[84] The potassium atoms are located nearly midway between oxygen atoms at a spacing of 2·8 A.[83,85]

When cooled below 122°K., primary potassium phosphate undergoes a transition to a ferroelectric modification.[87] The temperature at which this transition occurs has been determined as 121·97°K., but it is more probable that the change occurs continuously over a small range of temperature rather than discontinuously at an exact point.[88,89] Mixed crystals of primary potassium phosphate with thallium ion show a higher temperature of transition.[90] Below the transition temperature, primary potassium phosphate changes to a crystal hybrid, in which there is a break up of the single crystal into subcrystalline regions.[89,91] These subcrystalline units have only a slightly different structure and can fit into the original crystal lattice without great strain. No breakdown of the original crystal to powder takes place, and when the hybrid crystal is warmed above the transition temperature the subcrystalline units merge after varying periods of time into the original lattice.[89] This reversible change can be repeated indefinitely by heating and cooling the crystal. The subcrystalline units are oriented in a definite way with respect to the original crystal and the *c*-axis becomes electrically polarised below the transition temperature.[87,89,92,93] The transition is similar to that which takes place in Rochelle salt to cause the formation of a domain structure.[94-96] *X*-Ray studies of crystals of primary potassium phosphate below 122°K. have shown splitting of the reflected *X*-rays from lattice planes having different lattice constants.[89,97,98] The linear dimensions of the subcrystalline units have been found to lie between 10^{-1} and 10^{-4} cm.[87] The nature of the transition at 122°K. is believed to be associated with the orientation of the hydrogen bonds in the crystal.[88] A theory put forward by Slater explains the transition by the tendency of $(H_2 - PO_4)^-$ dipoles to become oriented, pointing along the axis of the crystal in their positions of lowest energy. This would give rise to a tendency for spontaneous polarisation along this axis, as occurs below the transition point.[99,100] This theory has been applied to the interaction of all the atoms in the crystal, but has been considered to operate only as a second-order effect if the temperature is below that at which free rotation of the molecules begins.[101,102] It seems probable that the orientation of hydrogen bonds does occur, but that it does so in conjunction with other structural changes.[82] Below 122°K., the unit cell of primary potassium phosphate changes to an orthorhombic form having the space group *Fdd*.[82,87] Neutron diffraction studies have shown that the arrangement of the hydrogen atoms in the ferroelectric modification is ordered and that the PO_4 groups are regular tetrahedra.[103,82,104] The hydrogen atom may occupy either of two positions of minimum energy along the O–H–O bond and may move from one position to the other on reversal of an applied electric field.[105,104] The positions of these minima are ± 0·18 A. from the centre of the O–H–O bond, which is 2·50 A. in length.[103-105] Tabulations of interatomic distances and lattice dimensions for primary potassium phosphate above and below the transition temperature show that the H-bond contracts markedly between room temperature and 126°K., and then, below the transition temperature, an expansion occurs at 116°K.[82] Various studies have been made of the deuterium analogue of primary potassium phosphate. The replacement of hydrogen by deuterium causes the temperature of the ferroelectric transition to change to 213°K.[87,88,106] This replacement also causes expansion of the crystal at right angles to the *c*-axis, which may be caused by expansion of the H-bonds on substitution.[107] The deuterium analogue forms monoclinic crystals.[107] The crystal axes have been given as:- $a = 7{\cdot}37 \pm 0{\cdot}01$ A., $b = 14{\cdot}73 \pm 0{\cdot}01$ A., $c = 7{\cdot}17 \pm 0{\cdot}01$ A., $\beta = 92°$. The space group is $C_2^2 - P2_1$.[107]

The specific volume of solutions of primary potassium phosphate has been determined at 25°C., 50°C. and 75°C. over the concentration range 1–150 moles per 1000 moles of water,[108] and the results appear in Table V.

TABLE V.- THE SPECIFIC DENSITY (d) AND THE SPECIFIC VOLUME (v) OF SOLUTIONS OF KH_2PO_4

Temp. °C.	Concentration of KH_2PO_4 Mol. per 1000 mol. of water	Mol. per 1000 g. of water	Mol. per 1 litre of solution	% by weight	d	v
25	1·0	0·0555	0·0552	0·7502	1·00235	0·99765
25	2·5	0·1388	0·1376	1·8546	1·01005	0·9900
25	5·0	0·2775	0·2735	3·642	1·0227	0·97785
25	10·0	0·5551	0·5404	7·027	1·0470	0·9551
25	20·0	1·1101	1·0537	13·131	1·09275	0·9151
25	25·0	1·3877	1·3008	15·893	1·1142	0·8975
25	30·0	1·6652	1·5405	18·484	1·1349	0·8811
25	40·0	2·2203	2·0001	23·215	1·1737	0·8520
50	1·0	0·0555	0·0547	0·7502	0·9932	1·0068
50	2·5	0·1388	0·1363	1·8546	1·0008	0·9992
50	5·0	0·2775	0·2710	3·642	1·0131	0·98705
50	10·0	0·5551	0·5361	7·027	1·0370	0·9643
50	20·0	1·1101	1·0452	13·131	1·0815	0·9246
50	40·0	2·2203	1·9827	23·215	1·1617	0·8608
75	1·0	0·0555	0·0540	0·7502	0·98005	1·0204
75	2·5	1·1388	0·1344	1·8546	0·9875	1·0127
75	5·0	0·2775	0·2673	3·642	0·99965	1·00035
75	10·0	0·5551	0·5284	7·027	1·0233	0·97725
75	20·0	1·1101	1·0302	13·131	1·0676	0·9366
75	40·0	2·2203	1·9558	23·215	1·14735	0·8716
75	60·0	3·3304	2·7867	31·201	1·2162	0·8222

A linear relation exists between the specific volume and the concentration of the solution when this is expressed as percentage by weight, as shown in Fig. 3.[108] A linear relation also exists between the specific volume and the heat capacity of solutions of primary potassium phosphate.[108]

The Mendeléev characteristic temperature at which the coefficient of thermal expansion of a solution becomes equal to that of water has been found to be near 50°C. for solutions of primary potassium phosphate.[109]

Values of the heat capacity of solutions of primary potassium phosphate at 18°–20°C., given by Perreu, are shown in Table VI.[110] An equation to represent the specific heats found is given as:- $C_{p(18-20°)} = (7{\cdot}934 + h)/(15{\cdot}637 + h)$, where h is the number of moles of H_2O per mole of salt. Other workers have constructed isotherms for the variation of the specific heat of solutions of varying concentration of primary potassium phosphate at 25°C., 50°C. and 75°C.[111] Their results appear in Table VII. The partial molar heat capacity of the salt was positive at all the investigated concentrations of the solutions, while the partial molar heat capacity of water, $\bar{C}_{p_1}$, was lower than that of pure water $C^0_{p_1}$. The absolute value $\bar{C}_{p_1} - C^0_{p_1}$ increased with an increase of concentration and decreased with increasing

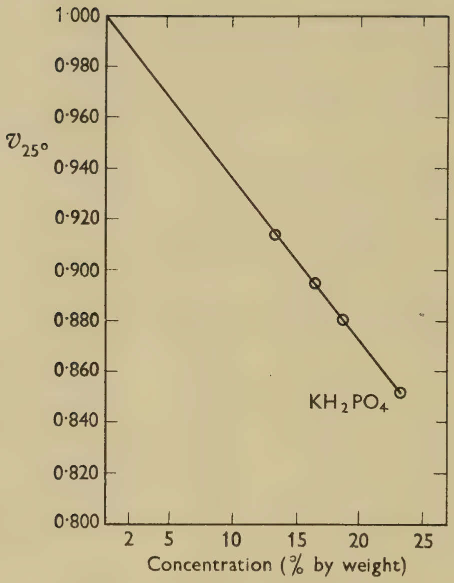

FIG. 3.- THE VARIATION OF THE SPECIFIC VOLUME OF KH_2PO_4 SOLUTIONS WITH CONCENTRATION

TABLE VI.- THE SPECIFIC HEAT CAPACITY (C_p) OF SOLUTIONS OF KH_2PO_4 AT 18–20°C.

p	*h*	*c*	C_p
0	∞	0	—
3	251·35	0·00396	0·972
6	125·93	0·00792	0·945
9	83·95	0·01189	0·922
12	62·96	0·01585	0·902
15	50·37	0·01981	0·885
18	41·97	0·02378	0·870
21·5 (sat.)	35·14	0·02832	0·856

Where: *p* = wt. in g. of KH_2PO_4 dissolved in 100 g. of water.
h = no. of g.-mol. of total water per g.-mol. of salt.
c = no. of g.-mol. of salt per g.-mol. of water.

TABLE VII.- THE SPECIFIC HEAT CAPACITY (C_p) OF KH_2PO_4 SOLUTIONS

$\frac{\text{mol. } KH_2PO_4}{1000 \text{ mol. } H_2O}$	No. of measurements	Temperature	C_p	Average deviation	Max. error
5	8	25°C.	0·9649	0·0010	0·10
10	11	25°C.	0·9313	0·0011	0·12
15	3	25°C.	0·9048	0·0005	0·06
20	11	25°C.	0·8797	0·0011	0·13
25	3	25°C.	0·8572	0·0009	0·11
30	6	25°C.	0·8367	0·0009	0·11
33·91	2	25°C.	0·8201	0·0005	0·06
40	2	25°C.	0·7996	0·0007	0·09

continued on following page

TABLE VII.- CONTINUED

$\frac{\text{mol. } KH_2PO_4}{1000 \text{ mol. } H_2O}$	No. of measurements	Temperature	C_p	Average deviation	Max. error
10	4	50°C.	0·9353	0·0007	0·08
20	6	50°C.	0·8838	0·0011	0·12
30	2	50°C.	0·8412	0·0005	0·07
40	6	50°C.	0·8055	0·0005	0·08
51·69	3	50°C.	0·7690	0·0008	0·11
10	3	75°C.	0·9392	0·0005	0·05
20	2	75°C.	0·8878	0·0004	0·05
40	2	75°C.	0·8126	0·0001	0·01

temperature, but remained negative even at 75°C.[111] Specific heats have also been determined for the system KH_2PO_4–$NH_4H_2PO_4$–H_2O at 25°C., 50°C. and 75°C., and these results are shown in Tables VIII–XII.[112]

TABLE VIII.- THE SPECIFIC HEAT CAPACITY OF SOLUTIONS IN THE SYSTEM KH_2PO_4–$NH_4H_2PO_4$–H_2O AT 25°C.

a_K	a_{NH_4}	No. of measurements	C_p (mean value)	Max. deviation from mean (%)
0	10	6	0·9496	0·1
2	8	2	0·9454	0·04
5	5	2	0·9412	0·09
8	2	7	0·9353	0·055
9	1	3	0·9334	0·065
10	0	11	0·9313	0·12
0	20	6	0·9069	0·11
5	15	4	0·9004	0·04
10	10	4	0·8932	0·10
15	5	6	0·8867	0·11
20	0	11	0·8797	0·11
0	30	5	0·8727	0·10
10	20	6	0·8605	0·10
15	15	2	0·8548	0·11
20	10	4	0·8481	0·06
30	0	6	0·8367	0·11
0	40	6	0·8445	0·10
10	30	2	0·8332	0·04
16	24	2	0·8260	0·10
30	10	6	0·8106	0·07
40	0	2	0·7996	0·09
0	50	2	0·8195	0·02
10	40	2	0·8100	0·01
20	30	2	0·8000	0·13
30	20	3	0·7900	0·08
33·2	16·8	2	0·7862	0·05
0	60	4	0·7976	0·09
10	50	2	0·7885	0·01
15	45	2	0·7830	0·01
20	40	2	0·7787	0·03
30	30	2	0·7692	0·01

continued on following page

TABLE VIII.- CONTINUED

a_K	a_{NH_4}	No. of measurements	C_p (mean value)	Max. deviation from mean (%)
10	60	2	0·7960	0·02
20	50	2	0·7605	0·01
28	42	2	0·7538	0·09
25	50	2	0·7467	0·03

a_K = number of mol. KH_2PO_4 per 1000 mol. H_2O
a_{NH_4} = number of mol. $NH_4H_2PO_4$ per 1000 mol. H_2O

TABLE IX.- THE SPECIFIC HEAT CAPACITY OF SOLUTIONS IN THE SYSTEM KH_2PO_4–$NH_4H_2PO_4$–H_2O AT 50°C.

a_K	a_{NH_4}	No. of measurements	Cp (mean value)	Max. deviation from mean (%)
0	20	4	0·9129	0·07
5	15	2	0·9062	0·07
10	10	4	0·8983	0·11
15	5	3	0·8918	0·06
20	0	6	0·8838	0·12
0	40	4	0·8518	0·04
10	30	2	0·8401	0·08
16	24	2	0·8340	0·09
20	20	2	0·8292	0·07
24	16	2	0·8247	0·03
30	10	3	0·8178	0·12
40	0	6	0·8056	0·08
0	60	2	0·8056	0·08
15	45	2	0·7901	0·05
20	40	2	0·7864	0·08
30	30	2	0·7764	0·09
40	20	2	0·7661	0·10
51	17	2	0·7441	0·09
0	75	2	0·7763	0·02
25	50	2	0·7542	0·03
0	80	2	0·7690	0·09
20	60	3	0·7521	0·08
32	48	2	0·7407	0·01
40	40	2	0·7347	0·02
48	32	2	0·7278	0·05
25	75	2	0·7164	0·08
40	60	2	0·7061	0·04
50	50	2	0·6987	0·03
19	96	2	0·7025	0·07
46	69	2	0·6880	0·07
30	90	2	0·6902	0·06
40	80	2	0·6850	0·09

a_K = number of mol. KH_2PO_4 per 1000 mol. H_2O
a_{NH_4} = number of mol. $NH_4H_2PO_4$ per 1000 mol. H_2O

TABLE X.- THE SPECIFIC HEAT CAPACITY OF SOLUTIONS IN THE SYSTEM KH_2PO_4–$NH_4H_2PO_4$–H_2O AT 75°C.

a_K	a_{NH_4}	No. of measurements	C_p (mean value)	Max. deviation from mean (%)
20	0	3	0·8878	0·05
10	10	2	0·9028	0·06
0	20	2	0·9172	0·03
40	0	2	0·8126	0·01
20	20	2	0·8354	0·08
—	40	2	0·8587	0·07
30	30	3	0·7824	0·05

a_K = number of mol. KH_2PO_4 per 1000 mol. H_2O
a_{NH_4} = number of mol. $NH_4H_2PO_4$ per 1000 mol. H_2O

TABLE XI.- THE SPECIFIC HEAT CAPACITY OF, AND TOTAL SALTS IN, SATURATED SOLUTIONS IN THE SYSTEM KH_2PO_4–$NH_4H_2PO_4$–H_2O AT 25°C.

a_K	a_{NH_4}	Amount of the salts Σa	C_p
33·91	0	33·91	0·8201
34·5	10·0	44·5	0·794
34·0	20·0	54·0	0·778
33·5	23·5	57·0	0·772
32·0	30·0	62·0	0·766
31·5	31·5	63·0	0·762
30·0	36·5	66·5	0·757
29·0	39·2	68·2	0·755
28·7	40·0	68·7	0·755
26·2	46·2	72·4	0·750
22·5	52·5	75·0	0·748
20·0	55·0	75·0	0·752
18·0	56·3	74·3	0·754
15·0	59·0	74·0	0·756
10·0	62·0	72·0	0·766
0	65·36	65·36	0·7878

a_K = number of mol. KH_2PO_4 per 1000 mol. H_2O
a_{NH_4} = number of mol. $NH_4H_2PO_4$ per 1000 mol. H_2O

TABLE XII.- THE SPECIFIC HEAT CAPACITY OF, AND TOTAL SALTS IN, SATURATED SOLUTIONS IN THE SYSTEM KH_2PO_4–$NH_4H_2PO_4$–H_2O AT 50°C.

a_K	a_{NH_4}	Amount of the salts Σa	C_p
51·69	0	51·69	0·7690
51·4	8·5	59·9	0·756
51·1	20·0	71·1	0·738
50·9	29·0	79·9	0·727
50·8	30·7	81·5	0·725
50·1	40·0	90·1	0·713
49·2	49·2	98·4	0·706
47·4	60·0	107·4	0·692
46·1	65·8	111·9	0·687
45·4	68·3	113·7	0·684

continued on following page

TABLE XII.- CONTINUED

a_K	a_{NH_4}	Amount of the salts Σa	C_p
40·7	80·6	121·3	0·683
40·3	81·0	121·3	0·683
40·0	81·8	121·8	0·683
30·9	92·7	123·6	0·685
30·0	93·2	123·2	0·686
20·0	99·7	119·7	0·694
0	102·7	102·7	0·7331

a_K = number of mol. KH_2PO_4 per 1000 mol. H_2O
a_{NH_4} = number of mol. $NH_4H_2PO_4$ per 1000 mol. H_2O

The integral heat of solution, *Lc* (g.-cal./mole), of primary potassium phosphate is given by the relation: $Lc = -4697 + 184{\cdot}3C - 12{\cdot}30C^2$ where the concentration, *C*, is expressed as moles of the salt per 100 moles of water.[12,113]

The chemical potential of water in aqueous solutions of primary and secondary potassium phosphates has been determined and discussed in terms of modern solution theory.[114]

The true melting point of primary potassium phosphate is difficult to determine owing to evolution of water vapour and condensation of the phosphate groups to polyphosphate species as the temperature approaches the melting point. Fusion of the salt has, however, been found to start at 252·6°C. and to be complete at 254·3°C.[115]

Primary potassium phosphate has a normal heat capacity of near 28 g.-cal./degree/mole at ordinary temperatures, but displays a pronounced electrocalorific effect at the upper Curie point of 122°K.[106,116-119] At this temperature a sharp maximum occurs, rising to a value of 160 g.-cal./degree/mole.[116-118] Apart from this peak at 122°K., the heat capacity varies linearly from 7 g.-cal./degree/mole to 18·5 g.-cal./degree/mole over the temperature range 40°K. to 130°K.[120] At 122°K., the spontaneous polarization, P_s, of primary potassium phosphate decreases rapidly to zero, and calculations of heat capacity changes in this range, using the P_s-temperature behaviour, agree well with experimental values.[121] The heat of transition and entropy change associated with the anomalous portion of the heat capacity curve have been found to be 87 ± 6 g.-cal./mole and 0·74 ± 0·06 g.-cal./degree/mole, respectively.[119] This agrees well with the theoretical entropy change calculated on the assumption that the H-bonds in the crystal cause the transition.[119]

The modulus of elasticity of primary potassium phosphate has been determined by a technique in which the resonance frequencies of crystals 3 × 5·5 cm. in size were measured.[122] At 20°C., the elasticity constants were found to be; $S_{11} = S_{22} = 1{\cdot}9$, $S_{33} = 2{\cdot}2$. Anomalies were found near the upper Curie temperature when the electrodes were in direct contact with the crystals, but not when an air space existed. Elasticity constants have also been determined for these crystals by an optical method down to −195°C.[123] These studies showed that two of the constants, C_{66} and C_{12}, decreased near the Curie point to about one sixth of their original values. The elasticity constants of the deuterium analogue have been determined over the temperature range −50°C. to 30°C. by a diffraction technique.[124]

The refractive index of solutions of primary potassium phosphate at 25°C., and for light of wave-length 589 mμ, may be found from the equation:- $n^{25}_D = AC + n'^{25}_D$ where *A* is a constant equal to $1{\cdot}056 \times 10^{-3}$, *C* is the concentration of the solution expressed as g. salt in 100 ml. of solution and n'^{25}_D is the refractive index of the water used to prepare the solution, measured at a wave-length of 589 mμ.[33]

The electro-optical Kerr effect in primary potassium phosphate has been studied over a range of temperatures. A discontinuous decrease in the double refraction occurs at the upper Curie point.[125] Similar effects occur with the deuterium analogue of primary potassium phosphate at its transition temperature of 213°K.[126] Above this temperature, the electro-optical double refraction of the substance is proportional to the strength of the electric field.[126]

The Raman spectrum of primary potassium phosphate has been studied using the 4358 A. line of mercury.[15,127,128] Ten Raman lines are assigned to internal vibrations of H_2PO_4, two to rotatory oscillations of H_2PO_4 groups, and three to a translatory type of external oscillation, in a spectrum excited by the 2537 A. mercury line incident upon a large crystal of primary potassium phosphate.[129] The infra-red absorption spectrum of primary potassium phosphate has been determined in the 650–4000 cm.$^{-1}$ region.[32]

Primary potassium phosphate displays the piezo-electric effect.[130] The piezo-electric modulus d_{36} varies with temperature and has been determined over the range 100–300°K.[131-134] At room temperature, a value of 5–6 × 10^{-7} e.s.u. per dyne has been found, while at the Curie point of 123°K. the value rises to about 6 × 10^{-4} e.s.u. per dyne.[131,135,136]

A value of 31 has been reported for the dielectric constant of primary potassium phosphate at room temperature, and this high value is attributed to the dipole character of the molecule in the crystal.[16] Several studies have been made of the variation of the dielectric constant with temperature. Lower values have been found for the dielectric constant of a clamped rather than a free crystal, and both increase as the temperature is lowered. This increase is shown, for a clamped crystal, in Table XIII.[134]

TABLE XIII.- THE DIELECTRIC CONSTANT OF CLAMPED CRYSTALS OF KH_2PO_4

Temperature		ϵ_k
°K.	°C.	
373	100	17·0
353	80	18·0
333	60	18·9
313	40	20·3
293	20	21·8
273	0	23·75
253	−20	26·0
233	−40	29·4
213	−60	34·9
193	−80	43·9
173	−100	57·6
153	−120	89·8
143	−130	123·0
133	−140	200·0
128	−145	291·0
123	−150	542·0

Measurements of the dielectric constant at 1 kc. for a free crystal and at 10 Mc. for a clamped crystal, have shown that plots of temperature against the reciprocal of the dielectric constant are linear for both cases. This is shown in Fig. 4.[143] With the free crystal, the temperature intercept occurs at the Curie temperature, and it is about 4° lower for the clamped crystal.

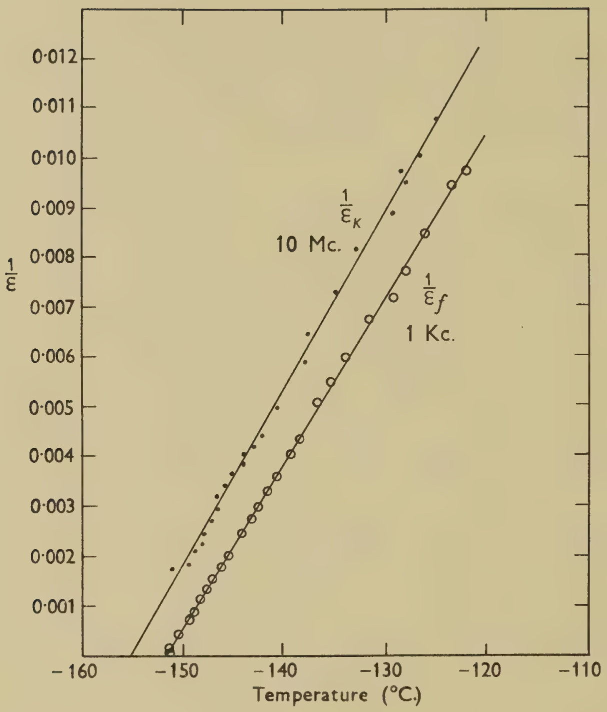

FIG. 4.- THE DIELECTRIC CONSTANT OF CRYSTAL PLATES OF KH_2PO_4
ϵ_f = DIELECTRIC CONSTANT OF FREE CRYSTALS
ϵ_k = DIELECTRIC CONSTANT OF CLAMPED CRYSTALS

The dielectric constant normally given for primary potassium phosphate is that measured along the direction of the *c*-axis of the crystal. The dielectric constant measured in the direction of the *a*-axis displays less variation with temperature, as may be seen from Fig. 5.[142] As the temperature is lowered, one maximum value of the dielectric constant is found at the Curie temperature.[17,137-139] Values of the effective dielectric constant of 32,000 have been found at this temperature.[134,140-142] A typical graph showing this behaviour appears in Fig. 6.[141] The dielectric constant drops rapidly below 70°K. and below 50°K. it has the same value as at room temperature.[140,141] The transition point may be determined from the variation of the dielectric constant with temperature.[144] The changes in the dielectric properties of primary potassium phosphate and the polarisation of the substance around the Curie temperature may be due to the displacement of H^+ ions in the crystal.[34,145-148] Equations have been derived to relate the polarisation of the substance to various thermodynamic properties.[149] Small crystals do not display spontaneous polarisation at low temperatures if their size is below a critical diameter of about 1500 A.[150,151] This effect is related to the dielectric properties of the medium surrounding the crystals, and if this is a conductor, particles as small as 500 A. show normal spontaneous polarisation.[152] In the presence of an electric field, the dielectric polarisation of primary potassium phosphate does not vary linearly with field strength, but displays a saturation and hysteresis effect.[131,153-155] The dielectric loss of primary potassium

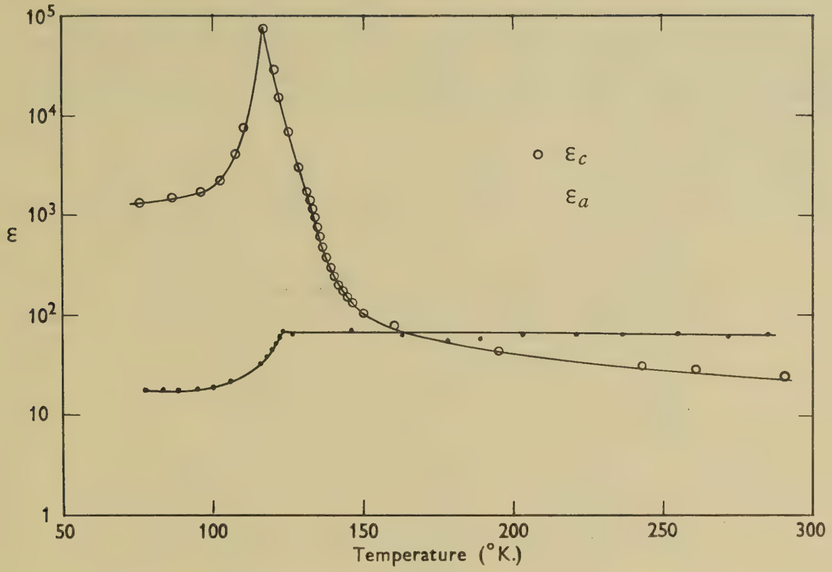

FIG. 5.- THE DIELECTRIC CONSTANTS OF KH_2PO_4 MEASURED AT 800 CYCLES/SECOND WITH FIELD INTENSITY OF 200 VOLTS/CM.

ϵ_c = THE DIELECTRIC CONSTANT IN THE DIRECTION OF THE c-CRYSTAL AXIS.
ϵ_a = THE DIELECTRIC CONSTANT IN THE DIRECTION OF THE a-CRYSTAL AXIS.

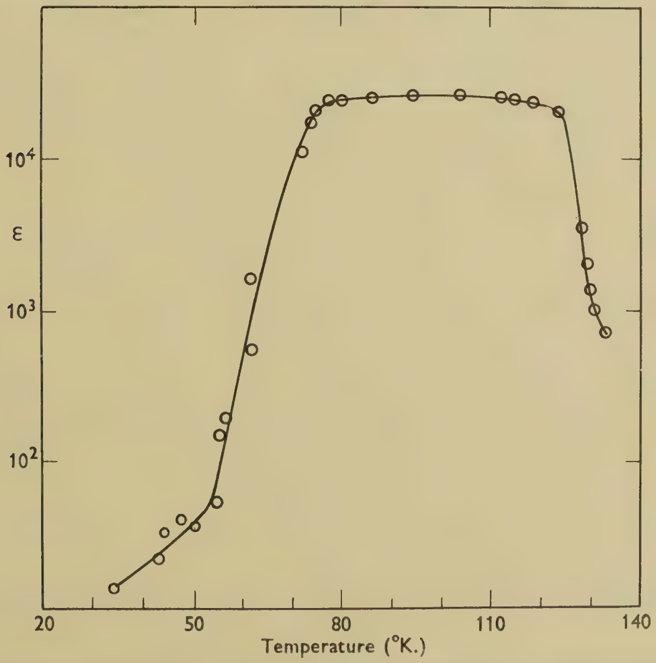

FIG. 6.- THE VARIATION WITH TEMPERATURE OF THE DIELECTRIC CONSTANT OF KH_2PO_4 NEAR THE CURIE POINT, MEASURED AT 50 CYCLES/SECOND WITH FIELD INTENSITY OF 2,400 VOLTS/CM.

phosphate occurs suddenly at the Curie temperature and, with further lowering of temperature, it reaches a maximum at the point where the dielectric constant decreases.[141] The dielectric loss is increased at low frequencies by grinding the substance.[156] The electrical conductivity of primary potassium phosphate is first increased by grinding the substance, but later falls slightly, as shown in Fig. 7.

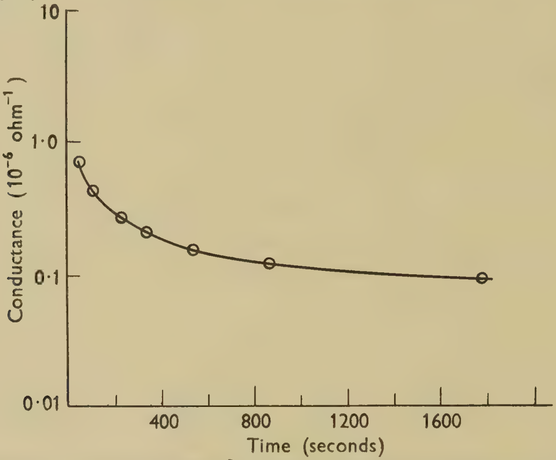

FIG. 7.- EFFECT OF GRINDING ON THE CONDUCTANCE OF KH_2PO_4 AT 16KC./S. ($0{\cdot}022 \times 10^{-6}$ OHM^{-1} BEFORE GRINDING).

The effect of highly conducting regions at the crystal surfaces, due to adsorbed layers of water, is believed to contribute largely to the electrical conductivity of the substance. It is suggested that when the crystals are ground, water held within them, possibly in small cracks, is released and distributes itself over the newly formed surfaces with a resultant increase of electrical conductivity. Evaporation of some of this water then causes the slight decrease of conductivity.[156] The electrical conductivity of the salt at room temperature has been measured in the pressure range 1400–21,000 kg./sq.cm. with the result shown in Fig. 8.[157]

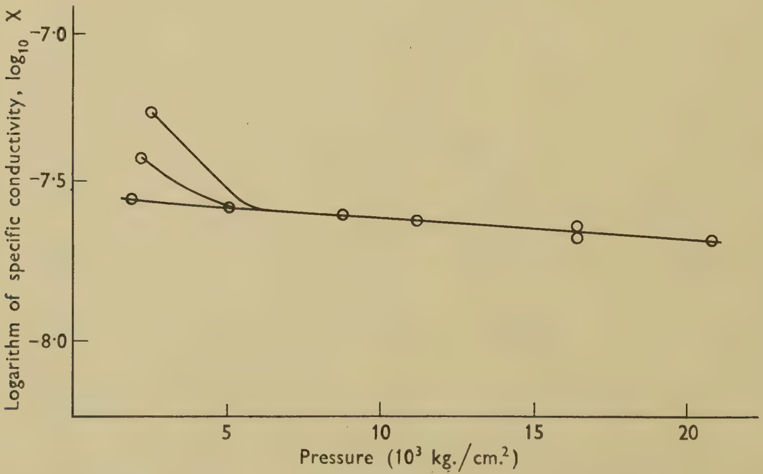

FIG. 8.- VARIATION OF THE LOGARITHM OF THE SPECIFIC CONDUCTIVITY OF THREE SPECIMENS OF KH_2PO_4 WITH APPLIED PRESSURE.

Primary potassium phosphate does not form hydrates, but an unstable compound of the composition KH_2PO_4,H_2O_2 or $KH_2PO_4,1{\cdot}25H_2O_2$ has been prepared by the evaporation at room temperature of solutions of the salt in hydrogen peroxide solutions.[31,158] Various determinations of the solubility of the salt in water have been made.[31,159-163] The general solubility equation for the salt has been given as $a = 12{\cdot}79 + 0{\cdot}250t + 0{\cdot}00182t^2 - 0{\cdot}00000616t^3$, where a is the number of grams of salt dissolving in 100 g. of solution at t°C.[163] In Table XIV are shown values calculated from this equation for the solubility at various temperatures of primary potassium phosphate, together with experimentally determined values.[163]

TABLE XIV.- THE SOLUBILITY OF KH_2PO_4 IN WATER

Temperature °C.	g. KH_2PO_4 per 100 g. solution	
	Calculated	Determined
−2·75	12·09	—
0	12·79	12·88
5	14·05	14·00
7	14·63	—
10	15·46	15·50
15	16·93	16·87
18	17·84	—
20	18·46	18·45
23	19·44	—
25	20·09	20·04
30	21·77	21·90
35	23·51	23·65
40	25·31	25·10
45	27·17	26·90
50	29·07	29·00
60	33·01	33·40
70	37·10	37·05
80	41·29	41·30
83	42·64	—
90	45·53	45·5

In solutions of phosphoric acid, KH_2PO_4,H_3PO_4 is formed, which is more soluble than primary potassium phosphate itself.[159,160] This may be seen from the phase diagram in Fig. 9, which appeared in a recent review on alkali orthophosphates,[4] and which is based mainly on the work of Berg and Ravich.[164,37] Studies of the system KH_2PO_4–$NH_4H_2PO_4$–H_2O over the temperature range −4·45°C. to 40°C. have shown that these two salts form a continuous series of solid solutions.[158] No compounds between urea and primary potassium phosphate have been observed in studies of solutions of these substances in the range −12·9°C. to +35°C.[165] A triple eutectic is formed at −3·3°C. with boric acid, having the composition 11·7% KH_2PO_4 + 2·6% H_3BO_3 +85·7% H_2O.[161,166] No solid solutions or double salts were found in studies of solutions of primary potassium phosphate and potassium sulphate.[162] Double phosphates of calcium and potassium are found in the system $Ca^{++} - K^{+} - H^{+} - PO_4^{---} - H_2O$.[160] The solubility of primary potassium phosphate is only slightly altered by saturating the solution with potassium chloride.[159]

Various studies have been made of the course of the thermal dehydration of primary potassium phosphate. Although early reports stated that the acid pyrophosphate and trimetaphosphate could be made by heating primary potassium phosphate, this has not been confirmed by later work.[167,168] Complete dehydration to potassium metaphosphate occurs when primary potassium phosphate is heated for 6–7 hr. at 245°C.[40] The rate of dehydration of the ortho-

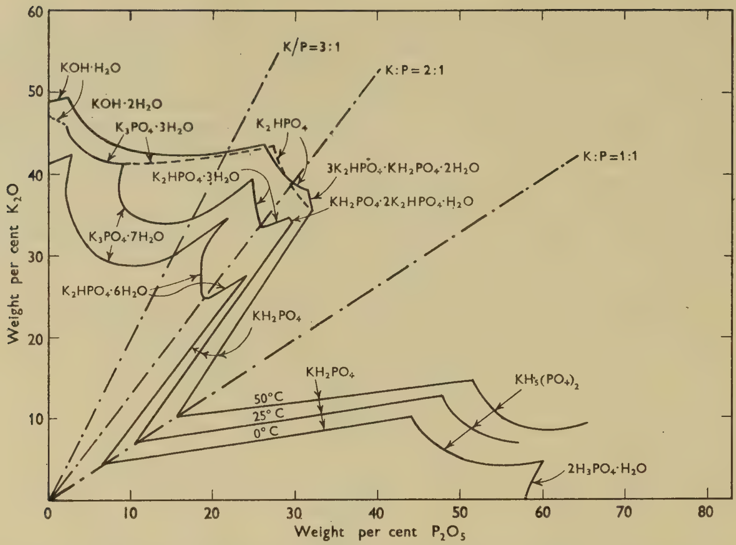

FIG. 9.- THE SYSTEM K_2O–P_2O_5–H_2O AT 0°C., 25°C. AND 50°C.

phosphate becomes appreciable at 208°C. and rapid at 258°C.[40] There is some disagreement about the nature of the substances formed during the thermal dehydration of primary potassium phosphate. Some reports state that acid pyrophosphates and triphosphate are formed at various temperatures together with double salts of the orthophosphate and pyrophosphate.[169-171] Other workers claim, however, that no pyrophosphate is formed as an intermediate in the dehydration and that only potassium metaphosphate can be made in this way.[40,172,173] It may be concluded that only insoluble potassium metaphosphate can be prepared easily by the thermal dehydration of primary potassium phosphate. In preparing this substance, it is desirable to heat the product to 500°C. for about 30 min. to ensure complete dehydration. Mixtures of condensed phosphates of varying complexity can be formed, however, by heating primary potassium phosphate at temperatures of 200°C.–300°C. for periods of time sufficient to cause only partial dehydration. There is evidence that some potassium acid pyrophosphate, $K_2H_2P_2O_7$, may be formed in this way.[170] This substance cannot be made in good yield by this technique, however, because its dissociation pressure at these temperatures is very nearly the same as that of primary potassium phosphate, as may be seen from Tables XV and XVI.[174] This is an important difference from the sodium system, in which the acid pyrophosphate may readily be prepared by thermal dehydration of primary sodium phosphate. The rate of dehydration of primary potassium phosphate is increased considerably by a reduction of pressure.[172,175] Thus, potassium metaphosphate can be made by heating primary potassium phosphate for several hours at 220°C. in a vacuum, whereas a temperature near 370°C. is required for rapid formation of the metaphosphate at atmospheric pressure.[170]

Primary potassium phosphate reacts with the secondary salt when intimate mixtures of the two are heated. Two reactions have been said to occur:-[40]

$$K_2HPO_4 + KH_2PO_4 \rightarrow K_3HP_2O_7 + H_2O$$
$$\text{and } K_3HP_2O_7 + K_2HPO_4 \rightarrow K_5P_3O_{10} + H_2O$$

The first reaction occurred at 245°C., and the second at 325°C. In the absence of an excess of the secondary salt, a third reaction could take place at higher temperatures:-[40]

$$2K_3HP_2O_7 \rightarrow KPO_3 + K_5P_3O_{10} + H_2O$$

TABLE XV.- THE EQUILIBRIUM PRESSURE OF THE SYSTEM $x\,K_2H_2P_2O_7 \rightleftharpoons 2(KPO_3)_x + x\,H_2O$

Temperature °C.	Average pressure (mm. Hg)	Number of measurements
165·0	19·5	1
167·0	21·2	1
170·0	24·3	5
180·0	42·9	5
186·5	58·8	1
190·0	64·3	4
190·5	68·1	2
200·0	98·3	13
202·0	104·4	1
210·0	135·9	3
211·0	145·5	1
212·0	149·3	2
220·0	203·1	2
230·0	309·1	6
240·0	469·4	6
250·0	634·3	3
260·0	734·8	3

TABLE XVI.- THE EQUILIBRIUM PRESSURE OF THE SYSTEM $x\,KH_2PO_4 \rightleftharpoons (KPO_3)_x + x\,H_2O$

Temperature °C.	Average pressure (mm. Hg)
170·0	6·3
180·0	25·5
191·0	46·5
200·0	68·3
210·5	118·7
220·0	188·3
230·0	306·5
240·0	467·9
250·0	673·3
254·5	715·8
254·8	721·2
255·5	728·2
256·5	733·6
257·0	734·9
258·5	739·1
264·0	751·0

The applications of primary potassium phosphate include its use in agricultural fertilisers, where its lack of hygroscopicity is of value.[73,176-178] The substance has also been used as a constituent of catalysts for the hydrogenation of carbon monoxide.[179,180] The piezo-electric properties of crystals of primary potassium phosphate make it useful for the construction of crystal filters and frequency stabilizers in electronic circuits.[50,181,182] Solutions for use as pH standards are prepared using mixtures of primary potassium phosphate and secondary sodium or potassium phosphate.[183-185]

A 1·0 M. solution of primary potassium phosphate can react with kaolinite at 90°C. to form a compound of the composition $KOH(Al)_2(PO_4)_2, 1{\cdot}7H_2O$.[186]

POTASSIUM PYROPHOSPHATES

Normal potassium pyrophosphate, $K_4P_2O_7$, can be prepared by the thermal dehydration of secondary potassium phosphate. Studies of this dehydration have shown that it proceeds in two steps, the first starting at 282°C., and the second around 400°C.[40] A period of several hours heating at 700°–800°C. is desirable in the preparation of the normal pyrophosphate by this method. Both normal potassium pyrophosphate and the acid salt, $K_2H_2P_2O_7$, can be prepared by causing a cold solution of potassium hydroxide to react with crystallised pyrophosphoric acid.

Potassium pyrophosphates can be made by heating mixtures of a phosphorite and potassium carbonate to temperatures near 1000°C.[187] A method has also been described for making the normal pyrophosphate by heating potassium chloride with primary potassium phosphate or potassium ammonium phosphate.[188]

Potassium acid pyrophosphate forms a hemihydrate, $K_2H_2P_2O_7,0{\cdot}5H_2O$, which is monoclinic, with space group $C2/c$.[189] There are eight molecules in the unit cell, which has the dimensions $a = 17{\cdot}92$ A., $b = 7{\cdot}01$ A., $c = 14{\cdot}27$ A., $\beta = 120{\cdot}7°$.[189]

The infra-red absorption spectrum of normal potassium pyrophosphate in the 650–4000 cm.$^{-1}$ region is shown in Table II.[32] The refractive index of solutions of normal potassium pyrophosphate at 25°C., and for light of wavelength 589 mμ may be found from the equation:-

$$n_D^{25} = 1{\cdot}376C + n'^{25}_D$$

where C = no. of g. of the salt in 100 ml. of solution and n'^{25}_D is the refractive index of water at 25°C. and 589 mμ.[33]

The dissociation pressure of potassium acid pyrophosphate has been determined over the temperature range 165°–260°C. and values are given in Table XV.[174] The salt rapidly loses its water of constitution at 250°C. and is quickly transformed into potassium metaphosphate at higher temperatures.[172]

Studies have been made of various binary systems involving normal potassium pyrophosphate. A eutectic is formed with potassium tungstate having a melting point of 836°C. and a composition of 34·5% normal potassium pyrophosphate.[190] An unstable system is formed with barium titanate and displays a minimum melting point of 992°C. at a composition of 11 mole-% of the barium salt.[191],[192] With lead titanate, a minimum melting point of 962°C. occurs at the composition 12·5 mole-% of the lead salt.[193] With potassium fluoride, normal potassium pyrophosphate forms a eutectic at 712°C. and a compound $3KF,K_4P_2O_7$, m.p. 812°C.[191] Normal potassium triphosphate is the stable crystalline phase in contact with liquid in the system with potassium metaphosphate, over the composition range from 0·375 mole fraction P_2O_5 up to the eutectic between the metaphosphate and normal potassium pyrophosphate, (see Fig. 10).[194] A continuous series of solid solutions is formed by the normal pyrophosphates of sodium and potassium.[195] Studies of the binary systems formed from normal potassium pyrophosphate and potassium sulphate, potassium chromate, potassium molybdate and potassium tungstate showed no evidence of complex formation and gave only simple eutectics.[196]

Normal silver pyrophosphate has an appreciable solubility in solutions of normal potassium pyrophosphate, and the solubility increases with increasing concentration of the potassium salt.[197]

One of the most extensive applications of normal potassium pyrophosphate is as a constituent of both solid and liquid detergents.[198-201] The potassium and phosphorus in the salt are readily available to plants, but the salt has little application as a fertiliser.[202] It has been used as a constituent of

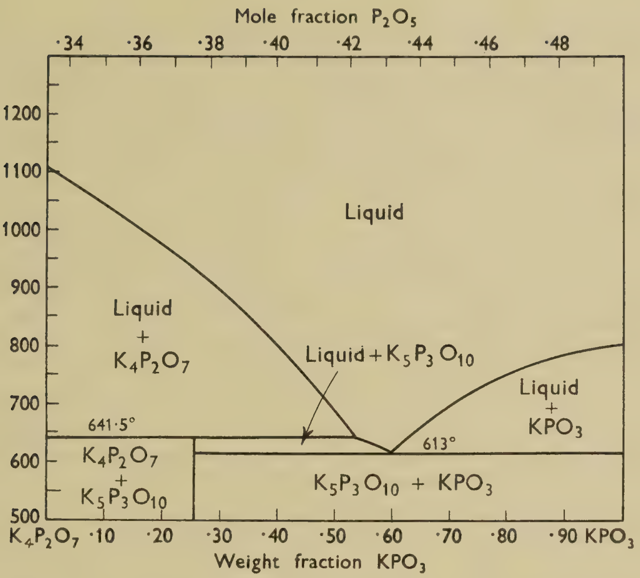

FIG. 10.- THE PHASE EQUILIBRIUM DIAGRAM OF THE BINARY SYSTEM $K_4P_2O_7$–KPO_3

various oxidation-reduction systems in high polymer syntheses[203,204] and in activators and catalysts for making synthetic rubber.[205,206] The substance is also used in preparing dispersions of certain dyes, prior to spray-drying to form finely divided powders.[207]

POTASSIUM METAPHOSPHATES AND POLYPHOSPHATES

Insoluble potassium metaphosphate, sometimes called potassium Kurrol salt, may be prepared by thermal dehydration of primary potassium phosphate.[208,209] Various temperatures and times of heating have been used, up to 30 minutes' heating at 900°C.[210] At temperatures above 500°C., periods of 30 min. heating are sufficient to cause complete dehydration of the orthophosphate.[40] Starting from sodium Maddrell salt, a water-soluble, uniformly polymeric potassium metaphosphate has been made by treating the sodium salt with the hydrogen form of an ion-exchange resin in aqueous suspension. The resulting solution of the free acid is then treated with potassium hydroxide and alcohol to precipitate potassium metaphosphate.[211]

Normal potassium triphosphate melts incongruently at 641·5°C. to form pyrophosphate and liquid, as may be seen from the phase diagram in Fig. 10.[194] The salt can be made similarly to the normal sodium triphosphate by heating a mixture of the primary and secondary orthophosphates in proportions to give the correct alkali to phosphorus ratio. The mono- and dihydrates of the acid triphosphate $K_3H_2P_3O_{10}$ have been prepared by treating a cold, saturated solution of the normal salt with glacial acetic acid followed by the addition of alcohol.[212]

Insoluble potassium metaphosphate can be made on a laboratory or larger scale by reaction between phosphoric acid and potassium chloride.[57,213,214] This reaction has been studied by various workers, and it has been shown that potassium metaphosphate can be formed at temperatures above 300°C.[215,216] Reaction temperatures in the region of 700°–900°C. have been employed in some cases in order to ensure complete elimination of chlorine as hydrogen chloride.[213,215] Chloride-free products can be obtained at much lower reaction temperatures, however, if an excess of phosphoric acid is used. In general, it has been found that chloride elimination can be achieved at moderate reaction temperatures with an excess of acid present, but if equimolecular proportions of the reactants are used, very high temperatures, with fusion of the reaction mass, are needed to eliminate all the chloride from the system. This can depend to a large extent upon the technique used, and complete reaction of the chloride can be achieved using equimolecular proportions of the reactants if they are applied to a moving bed of particles of the product heated to a temperature around 500°C.[217] The reaction has also been carried out by treating finely divided potassium chloride with concentrated phosphoric acid in a vacuum at temperatures up to 250°C.[218] Mixed phosphates of sodium and potassium have been prepared in water-soluble form by heating together potassium chloride, sodium chloride and phosphoric acid.[219,220] A process for preparing potassium metaphosphate from potassium chloride and primary ammonium phosphate involves heating a mixture of these powders progressively to 675°C. during 2–3 hr.[221] Potassium metaphosphate has also been made by reaction between potassium polysilicates and calcium phosphates.[222]

The unit cell of the insoluble, polymeric, potassium metaphosphate, $(KPO_3)_n$, is monoclinic and has the dimensions $a = 14{\cdot}02$ A., $b = 4{\cdot}54$ A., $c = 10{\cdot}28$ A. and $\beta = 78$–79°.[209,223] The space group has been given most recently as $P2_1/a$,[223] although other space groups which have been suggested are $C_{2h}^5 - P2_1/c$, $C_{2h}^4 - P2/c$ and $C_s^2 - P_c$.[209] The microcrystalline structure of insoluble potassium metaphosphate has been described, together with the microscopic characteristics of several condensed phosphates of sodium.[224] The density of insoluble, polymeric potassium metaphosphate has been determined as 2·43 g./c.c.[223]

The solubility of pure, polymeric potassium metaphosphate in water alone is very low, and has been reported as less than 0·004 g. per 100 ml. at 25°C.[215] Its solubility is greatly increased in dilute solutions of various metallic cations other than potassium ions, which depress its solubility. Particularly effective in causing increased solubility of potassium metaphosphate are the cations of the alkali and alkaline earth metals, and ammonium.[225–228] The effects of a few of these salts are shown in Figs. 11 and 12.[225] Polymeric potassium metaphosphate can be dissolved completely in dilute salt solutions of this sort, and in the case of dissolution by dilute solutions of sodium salts, quantities up to 3·5 equivalents of sodium ion have been found to be required to dissolve one equivalent of potassium metaphosphate.[225,229,230] In the case of potassium metaphosphate made by the thermal dehydration of analytical grade primary potassium phosphate at 500°C., 2·5 to 3·0 equivalents of sodium ion are needed, and it is probable that differing reports of the quantity of sodium required result from the use of samples of potassium metaphosphate of varying degrees of polymerisation. The mechanism by which polymeric potassium metaphosphate is dissolved by dilute salt solutions has not been fully elucidated, but it is probable that a process of ion exchange is involved, and that colloidal, rather than normal electrolytic, solutions are formed.[227,229] The most extensive studies of the phenomenon of the dissolution of water-insoluble polymeric metaphosphates by dilute salt solutions have been made using metaphosphates of sodium, and extensive discussions of this subject are to be found in publications dealing with these substances.[1]

A water-soluble form of polymeric potassium metaphosphate can be made by stirring the insoluble compound in water with a cation exchange resin in its hydrogen form, and then treating the solution with potassium hydroxide after separating the resin.[231] The solution of potassium metaphosphate thus prepared should be free from foreign ions. Water-soluble forms of polymeric potassium metaphosphate can also be made by dissolving the insoluble

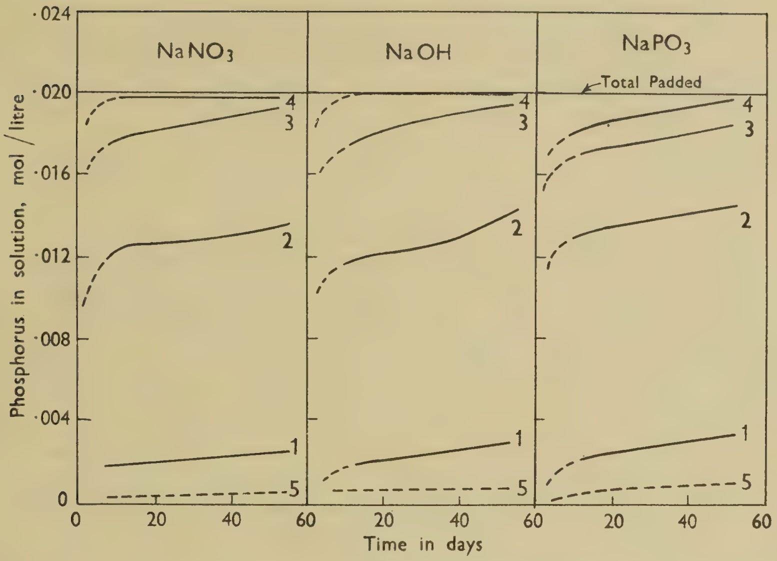

FIG. 11.- THE EFFECT OF SODIUM COMPOUNDS ON THE SOLUBILITY AND REVERSION OF 1·1812g. QUANTITIES OF KPO_3 IN 500 ML. OF SOLUTION (0·020 MOL./LITRE)

1 – NO SODIUM ADDED.
2 – 0·004 MOLS./LITRE Na ADDED.
3 – 0·010 MOLS./LITRE Na ADDED.
4 – 0·016 MOLS./LITRE Na ADDED.
5 – P IN SOLUTION AS ORTHOPHOSPHATE, 0·016 MOLS./LITRE Na ADDED.

compound in salt solutions such as 5% ammonium chloride, or in solutions of hydrogen peroxide, and then precipitating by adding alcohol.[208,232] Water-soluble forms of the substance have thus been obtained in the solid state, but are difficult to purify from contamination with the reagents used.

When polymeric potassium metaphosphate is dissolved by any of these methods, the resulting solutions have markedly increased viscosity. The extent of this increase depends upon the degree of polymerisation of the potassium metaphosphate, and this, in turn, depends upon the purity of the substance. Samples of highly polymerised potassium metaphosphate can yield dilute solutions of extremely high viscosity. Thus, a 0·1% solution of the substance can display self-siphoning behaviour, by flowing upwards to the edge of one vessel before passing over to another held below it.[233] The highly viscous solutions prepared from potassium metaphosphate have been used for the modification of film-forming and coating compounds and as suspending and dispersing agents.[226,231] They have also been used in the sizing of textile materials.[226] A mixture of equal weights of polymeric potassium metaphosphate and sodium metaphosphate (Graham's salt) dissolved in 5·5 parts by weight of water has been recommended as a highly viscous solution for use as a vehicle for ceramic pigments.[230] Various measurements have been made of the viscosity of potassium metaphosphate solutions with the object of determining the molecular weight of the substance. Some of these results are given in Tables XVII, XVIII and XIX.[227,234] The values obtained vary considerably, and molecular weights from 10^5 to over 10^6 have been reported.[227,232,234-236] It has been shown that the presence of a few p.p.m. of arsenic as impurity in the potassium metaphosphate results

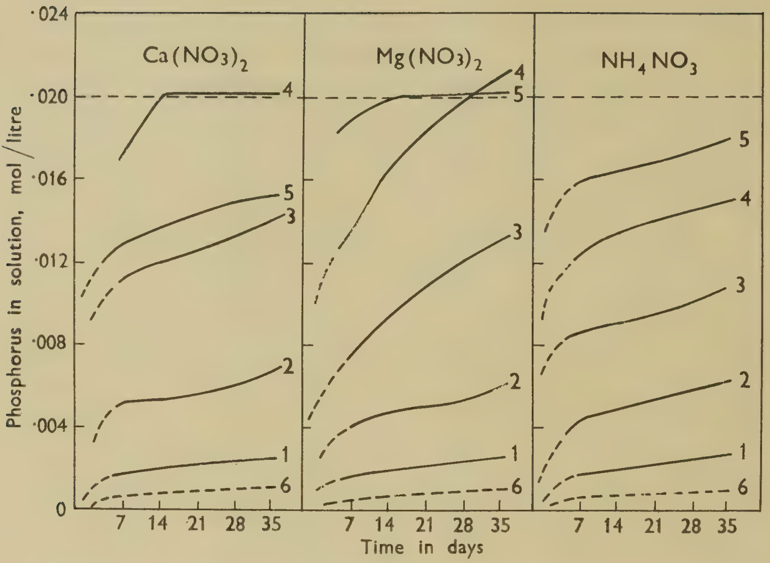

FIG. 12.- THE EFFECT OF $Ca(NO_3)_2$, $Mg(NO_3)_2$ AND NH_4NO_3 ON THE SOLUBILITY AND REVERSION OF 1·1812g. QUANTITIES OF KPO_3 IN 500 ML. OF SOLUTION (0·020 MOLS./LITRE).

1 – NO SALT ADDED.
2 – 0·001 N. SALT SOLUTION.
3 – 0·004 N. SALT SOLUTION.
4 – 0·010 N. SALT SOLUTION.
5 – 0·016 N. SALT SOLUTION.
6 – P IN SOLUTION AS ORTHOPHOSPHATE, 0·016 N. SALT SOLUTION.

TABLE XVII.- THE INTRINSIC VISCOSITY IN VARIOUS MEDIA OF $(KPO_3)_x$ MADE BY DEHYDRATION OF KH_2PO_4 AT 500°C.

Medium	$(\eta_{sp.}/C)_{c \to 0}$
0·4 M. NaCl (aqueous)	0·92
0·3 M. NaCl (aqueous)	2·30
0·2 M. NaCl (aqueous)	3·40
0·1 M. NaCl (aqueous)	5·20
0·1 M. NaCl (5% ethanol)	2·95
0·1 M. NaCl (8% ethanol)	2·00

TABLE XVIII.- THE VISCOSITY AND MOLECULAR WEIGHT IN 0·4 M NaCl SOLUTION OF SOME PREPARATIONS OF $(KPO_3)_x$ MADE BY DEHYDRATION OF KH_2PO_4

Temperature of synthesis (°C.)	$(\eta_{sp.}/C)_{c \to 0}$	Molecular weight
310	0·31	
335	0·33	300,000
425	0·55	
500	0·92	1,100,000
535	1·10	
585	1·13	
700	1·18	
725	1·34	

TABLE XIX.- THE SPECIFIC VISCOSITY AND DEGREE OF POLYMERISATION OF $(KPO_3)_x$ MADE BY DEHYDRATION OF KH_2PO_4

K/P ratio	Concentration of solution	Specific viscosity	Degree of polymerisation
1·01	1%	33·46	1150
1·00	10%	102·2	2400
1·05	1%	35·6	1200
1·01	1%	34·7	1180
1·00	1%	269·0	4200

in a reduction in the degree of polymerisation and a marked reduction in the viscosity of solutions of the substance.[235] This is believed to be due to greatly increased ease of hydrolysis of the metaphosphate chain at each position occupied by arsenic.[235] In the case of solutions of pure potassium metaphosphate, the energy of activation of the hydrolysis of the polymetaphosphate chain at pH 8·5 has been found to be about 25 kg.-cal./mole.[234]

The electrical conductivity of a solution of polymeric potassium metaphosphate has been found to be anisotropic when the solution is flowing. As is shown in Fig. 13, the greatest conductivity was found to occur in the direction of the flow, and the smallest in a direction perpendicular to the axis of flow.[237] Measurements of the conductivity of polymeric potassium metaphosphate in solutions of sodium thiocyanate have indicated about 30% dissociation of the metaphosphate, but the authors state that limitations of the method make this value unreliable.[236] Other determinations of the apparent dissociation of potassium metaphosphate in various media are shown in Table XX.[227]

TABLE XX.- THE PERCENT APPARENT DISSOCIATION (α) OF $(KPO_3)_x$ IN VARIOUS MEDIA

Temperature °C.	Medium	g. $(KPO_3)_x$ per litre	α
5	0·10 M Na Cl	5·00	12
20	0·40 M Na Cl	5·00	14
	0·20 M Na Cl	6·00	13
	0·10 M Na Cl	5·97	14
	0·05 M Na Cl	4·77	16
25	0·40 M Na Cl	8·77	16
	0·20 M Na Cl	6·30	14
	0·10 M Na Cl	5·07	16
	0·05 M Na Cl	4·32	16
35	0·40 M Na Cl	7·20	27

Solutions of polymeric potassium metaphosphate exhibit flow birefringence, and this has been measured for samples of various chain length dissolved in solutions of sodium salts and tetramethylammonium bromide.[238]

The infra-red absorption spectrum of normal potassium triphosphate has been determined in the 650–4000 cm.$^{-1}$ region, and is given in Table II.[32]

Several studies have been made of systems involving polymeric potassium metaphosphate and various other salts. Normal potassium triphosphate is a stable crystalline phase in a range of the system KPO_3–$K_4P_2O_7$, and in the system KPO_3–$NaPO_3$ the compound $3NaPO_3,KPO_3$ is formed.[194] The latter compound also appears in the system $NaPO_3$–$Na_4P_2O_7$–$K_4P_2O_7$–KPO_3, in which the compound $Na_5P_3O_{10},K_5P_3O_{10}$ may also be formed.[195] In the system KPO_3–$LiPO_3$, the compound $LiPO_3,KPO_3$ is formed, and eutectics occur at

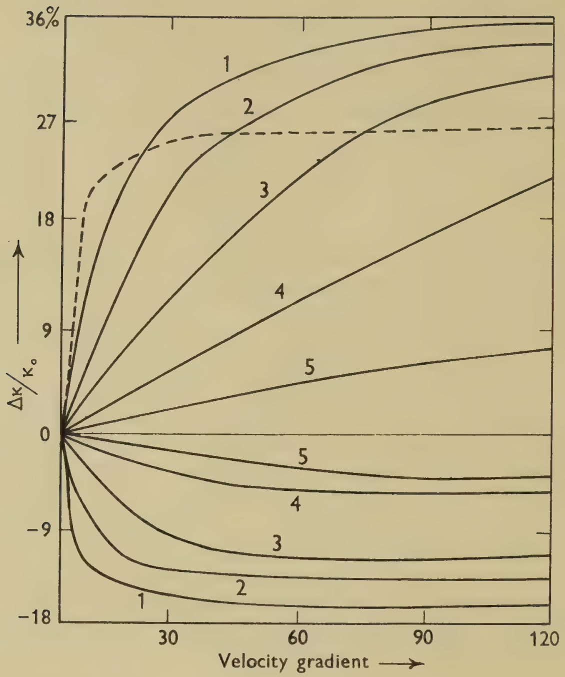

FIG. 13.- THE RELATIVE CHANGE OF CONDUCTIVITY $\Delta K/K_0 = \Delta x/x_0 = x - x_0/x_0$ (x = CONDUCTIVITY OF FLOWING SOLUTION, x_0 = CONDUCTIVITY OF STATIC SOLUTION) OF A POLYPHOSPHATE SOLUTION (MOL. WT. 660,000) IN RELATION TO THE MEAN VELOCITY GRADIENT AT VARIOUS CONCENTRATIONS (1 = $0{\cdot}8 \times 10^{-4}$, 2 = $3{\cdot}3 \times 10^{-4}$, 3 = $1{\cdot}05 \times 10^{-3}$, 4 = $3{\cdot}3 \times 10^{-3}$, 5 = $1{\cdot}2 \times 10^{-2}$ NORMAL).
The upper part of the figure shows the increasing conductivity in the direction of flow, while the lower part relates to the decreasing conductivity produced at right angles to the direction of flow. The curve shown as a dotted line represents the calculated increase in the portion of the conductivity of polyphosphate ions having a chain-length of 10,000 (mol. wt.~1,000,000).

528°C. and 518°C. with 37 and 64 mole-% $LiPO_3$.[239] The system KPO_3–Li_2SO_4 has eutectics at 569°C., 524°C., 582°C. and 502°C. with 26%, 40·5%, 55% and 80·5% Li_2SO_4, respectively, and forms the compound $(LiPO_3)_2,(KPO_3)_2$.[239, 240] The system KPO_3–$Na_2B_4O_7$ displays contraction for all concentrations of the borate from 16 to 64 mole-% over the temperature range 650°C. to 1200° C.[241] The system KPO_3–$BaTiO_3$ has melting point minima at 746°C., 747°C. and 776°C., with 11, 16 and 24 mole-%, respectively, of the barium salt.[192]

By using an ion exchange membrane to measure the ionic activity in solutions of electrolytes, the degree of dissociation of alkali metal polyphosphates has been found to decrease from potassium to sodium to lithium.[242] The anions of polymeric potassium metaphosphate in solution are believed to consist of long, unbranched chains of PO_4 tetrahedra.[243] The configuration of these chain polyanions may be altered by the presence of added salts.[238]

Both potassium trimetaphosphate and tetrametaphosphate yield the insoluble, polymeric metaphosphate when heated at temperatures above 250°C.[244-246] The dihydrate of the tetrametaphosphate loses its water of crystallisation at 100°C., and is partly transformed to a mixture of chain phosphates between 100°C. and 180°C.[244] Above 180°C., it yields polymeric potassium metaphosphate and the trimetaphosphate.[244] It has been reported that the transformation of trimetaphosphate to polymeric metaphosphate proceeds through the intermediate formation of tetrametaphosphate.[247]

Polymeric potassium metaphosphate reacts with the hydrogen form of an ion-exchange resin to form a solution of metaphosphoric acid.[211] Polymeric potassium metaphosphate can also react with a solution of ammonia to form an ammonium potassium phosphate.[248] It has been reported that potassium metaphosphate can be decomposed by hydrated or fused salts, such as the decahydrate of sodium sulphate, or fused potassium nitrate.[249]

Because of their lower price, the condensed phosphates of sodium are used much more extensively than those of potassium for purposes of detergency and sequestering. It has been shown, however, that potassium polyphosphates are generally at least as efficient as the sodium compounds in the preparation of detergents, and potassium metaphosphate has been found to be more effective than sodium metaphosphate for this purpose.[250-252] Potassium metaphosphate has also been claimed to be the best of a wide range of condensed phosphates studied for use in detergent formulations.[253] Owing to its insolubility, however, it must be used in admixture with another salt such as normal sodium pyrophosphate. Mixtures of sodium and potassium metaphosphate have also been employed in this way in synthetic detergents.[254]

Although potassium metaphosphate has never been put on the market as an agricultural fertiliser, the potassium and phosphorus in it are available to plants in the soil and the physical properties and high plant food concentration of the substance confer advantages in this application.[215] Generally, it has been found that the crop response to the phosphorus in potassium metaphosphate is equal to that in superphosphate.[255] This varies to some degree with the type of soil and some reports show a slight inferiority of potassium metaphosphate, while others claim that phosphorus from this source is absorbed by plants more readily than from superphosphate.[202,256] It has been found that potassium applied as potassium metaphosphate can be retained better by the soil than when applied as potassium sulphate.[257]

Other applications of insoluble potassium metaphosphate include its use to increase the viscosity of milk and milk products and as a thickening and stabilizing agent in these preparations.[258,259] In these applications it is usually mixed with a sodium salt, such as sodium citrate, to increase its solubility. When solubilized by admixture with sodium chloride, polymeric potassium metaphosphate has been treated with various dyes and used in non-inflammable moulding compositions and as additive for lubricating oils.[260] A potassium metaphosphate has been used in foundry work for the protection and refining of castings and to prevent the development of porosity.[261] Potassium metaphosphate has also been claimed to be a valuable lubricant for application to surgeons' rubber gloves.[262] The compound has been found to inhibit strongly the reaction of carbon black with potassium chlorate but to accelerate the reaction of graphite with it.[21] Potassium metaphosphate has been used in the preparation of flashless powders.[263] When traces of a compound of uranium are brought into solid solution with potassium metaphosphate by fusion, the substance is rendered luminescent under photo- or cathodo-excitation.[264]

MISCELLANEOUS PREPARATIONS OF TECHNICAL POTASSIUM PHOSPHATES

Numerous methods have been described for making potassium phosphates from tricalcium phosphate and from phosphate rocks. Feldspathic rocks and tricalcium phosphate may be caused to react together in an electric furnace to form potassium phosphate;[265] alternatively, tricalcium phosphate may be treated with a solution of potassium sulphate and sulphur dioxide.[266] Potas-

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sium phosphates intended for fertiliser purposes are made in various ways from phosphate rock. In one process,[267] crude calcium phosphate is treated with a mixture of sulphuric acid and ammonium sulphate solution. The filtered solution, containing phosphoric acid, is then neutralised with potassium hydroxide or carbonate and the calcium sulphate from the initial reaction is treated with carbon dioxide and ammonia to provide the ammonium sulphate for recycling. A solution of ammonium chloride has also been used to act upon phosphorites.[268] Several methods involving higher reaction temperatures have been described. A fused mixture of potassium chloride and apatite may be electrolysed in a special cell to form potassium phosphate near the iron cathode.[269] At temperatures around 1000°C. mixtures of a phosphorite and potassium carbonate react to form potassium phosphates substantially soluble in citric acid solution.[187] A plant with a capacity of 100 tons per day was built in the U.S.A. to make potassium phosphate for fertiliser purposes by fusing a slurry of phosphate rock and potassium carbonate in a rotary kiln.[270] Potassium phosphates suitable for fertilisers can be made by reaction between phosphate rock and various potassium minerals at temperatures ranging from 800°C. to 1300°C.[271,272] These reactants are ground to a fine powder before calcining and products almost entirely soluble in citric acid solution are formed. Another method claims that a product containing potassium and phosphorus in a form entirely available to plants can be made by sintering a phosphorite with pure potassium sulphate and charcoal at 1100°C. in the presence of air or water vapour.[273] Mixtures of potassium phosphates can be made for fertiliser purposes by causing potassium chloride to react with phosphoric acid. Using an excess of the acid, hydrogen chloride is readily driven off by heating to yield a solution from which salts, suitable as fertilisers, may be separated.[274,275] At higher temperatures, this reaction may be employed without excess of phosphoric acid to produce water-soluble, glassy mixtures of potassium phosphates.[219]

With calcium phosphate as starting material, a process has been devised in which conversion to the sodium salts is first achieved by elimination of calcium as sulphate or carbonate. Potassium phosphates are then formed by elimination of the sodium as sodium chloride.[276] Mixtures of potassium and ammonium phosphates may be separated by introducing ammonia into a solution or suspension of them in sufficient quantity to precipitate tri-ammonium phosphate without separation of potassium salts.[74]

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SECTION LIX

THE SPECTROSCOPY OF POTASSIUM AND CERTAIN OF ITS COMPOUNDS

By R. F. BARROW and LADY ANNE THORNE

THE SPECTRUM OF ATOMIC POTASSIUM

By A. THORNE

Introduction

The spectrum of atomic potassium has attracted much attention since the early days of spectroscopy, and indeed the study of the alkali-metal spectra played an important part in the development of modern spectroscopic theory. Brief historical accounts with references are given in most of the standard text-books on spectroscopy.[1-3,10,17]

A description of the potassium spectrum and its explanation in terms of modern theory is to be found in these and other text-books.[1-6] The neutral potassium atom has the ground-state electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s\ {}^2S_{1/2}$, with the $4s$ electron outside an argon-like core of closed shells giving rise to a doublet spectrum. The first doublet of the principal series lies in the near infra-red at 7665 A. and 7699 A. and the second in the violet at 4044 A. and 4047 A.; the rest of the principal series is in the ultra-violet. Most of the sharp and diffuse series lie in the visible, while the fundamental is in the infra-red. The most important energy levels and transitions of K I are shown diagrammatically by Grotrian.[7] Numerical values of experimentally determined energy levels of K I, II, III and IV have been tabulated by Bacher and Goudsmit,[8] and more recently and more comprehensively by the National Bureau of Standards for spectra up to K XI.[9]

Measured wave-lengths and intensities of spectral lines were first arranged in series by Fowler[10] and Paschen–Götze[11] for the K I spectrum. Later tables compiled by Moore[12,13] give multiplets of K I, II and III and some forbidden lines of K IV, V and VI from 13,000 A. to the far ultra-violet, together with a finding list arranged by wave-length. The M.I.T. wave-length tables,[14] which list the arc and spark lines of all elements between 10,000 A. and 2,000 A. in order of wave-length, include a list of the 'raies ultimes'; these are also given in the Vatican Observatory 'Atlas of Persistent Spectra'.[15] The use of certain potassium lines as reference lines in the near infra-red has been discussed.[16]

In 1938 Shenstone[17] published a summary of spectroscopic work on the arc and spark spectra of all elements, incorporating tables showing how thoroughly each spectrum had been investigated. Meggers[18] brought the information up to date in 1946, and at the same time Hartree[19] presented in a similar way a summary of the calculations of wave functions and energy levels.

Astrophysics.

Potassium lines of particular astrophysical interest are listed in Moore's multiplet tables.[12,13] In the case of the solar spectrum, tables of lines in the far infra-red region of the spectrum include several which have been ascribed to atomic potassium.[20-22]

K I lines have been identified in several stellar spectra,[23-30] and variations in their intensities have been studied.[23,24,26,30] Lines of ionized potassium have been found in certain nebulæ.[31-34]

Absorption lines due to potassium atoms in interstellar space have been investigated.[35-37]

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Excitation

The spectrum of potassium has been excited in flames, arcs, sparks and various forms of discharge and has been observed in absorption by several methods. In this section, reference is made only to those papers in which the conditions or mechanism of excitation has been the main consideration. Wave-length and intensity measurements on spectral lines, and specialized sources

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for particular investigations are described in later sub-sections. In particular, references to sparks are given in the sub-section on ionized potassium (see page 1994).

Flames, **Furnaces** and Collision **Processes.**

Many investigations have been made of the relation between the intensity of the spectral lines emitted from flame sources and the concentration of the potassium salts. This relation has generally been shown to follow a linear law at low concentrations and a square-root law at higher concentrations.[1-5,46] Different methods of introducing the salt into the flame have been described.[1,5,6] The distribution in the flame of the excited atoms[7,44,46] and the effect of adding other alkalies[8,9,45] have been studied. Reversal of the potassium resonance lines has been used to determine flame temperatures.[10,11]

In the electric furnace, lines have been observed in emission as well as absorption.[12]

Chemi-luminescence effects arising from the interaction of potassium vapour with the halogens have been investigated.[13-15] Excitation of the potassium spectrum by active nitrogen has been attributed to both chemi-luminescence and collision processes,[16,17,47] and attempts have been made to determine the form of collision process responsible for excitation by atomic hydrogen[18-20] and helium.[20]

Arcs.

The emission of potassium lines in arcs, including their spatial distribution, luminous duration, voltage and current dependence, etc., has been studied in some detail.[21-28] Work with aqueous solutions of salts has been described.[48] Spark lines have been found in both ordinary low-voltage[22] and interrupted[29] arcs. In view of the importance of the arc as a source in quantitative analysis, the intensity relations in a mixture of alkalies and the possibilities of the oscillating arc have been investigated.[30,31]

Discharges.

Arc and spark lines of potassium were early found in the negative glow of a discharge[32] and have also been studied in the positive column.[35] Relative intensities of the alkali-metal spectra in discharges passed through amalgams have been measured,[33,34] and lamps making use of sodium-potassium alloy have been described.[36,37] Both the arc and spark spectra of potassium have been brought out in electrodeless discharges.[38-43]

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The Spectrum of Neutral Potassium

The neutral potassium atom has the ground-state configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s\ {}^2S_{1/2}$, with an ionization potential of 4·339 V.[1] The latest determination[5] of the term value of the ground state is in good agreement with the value 35,009·78 cm.$^{-1}$ given in the National Bureau of Standards Tables.[1]

Moore's multiplet tables[2,3] list the first nine doublets of the principal series and a few members of other series with their term designations, intensities, references, etc. Fowler's tables,[4] incorporating earlier results,[6-8] give all the lines known at the time (1922), including 24 members of the principal series, 10 each of the sharp and diffuse, and several forbidden lines.

A complete list of experimentally determined energy levels is given in the National Bureau of Standards 'Atomic Energy Levels', published in 1949.[1] Term values are given for all excited states of the 4*s* electron up to 13*s*, 79*p*, 11*d*, 9*f*, 6*g* and 6*h*, respectively. These are based on Fowler's tables[4] with additions and modifications drawn from a few early observations in absorption,[9-12] later measurements of several more members of the sharp, diffuse and fundamental series[20-23] (including a few interferometric measurements),[24] and finally the extensive work of Kratz[25] on the principal series in absorption, which he has observed as far as $n = 79$. In 1956 the wave-lengths of 85 lines were measured or re-measured by Risberg,[5] using a hollow-cathode light source. He compiled a table of revised energy levels based on his measurements and computed Ritz–Rydberg formulae for the terms of all series; these agree well with his experimental values and with those of Kratz[25] for the principal series. The series limit found from Risberg's formulae is in excellent agreement with the value of 35,009·78 cm.$^{-1}$ found by extrapolating Kratz's measurements.

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Much attention has been devoted to iso-electronic sequences in the iron group, which begins with K I. The relations between their quantum defects, series limits, Ritz-Rydberg coefficients, and the appearance of 'raies ultimes' have been studied.[13-19,53]

Doublet intervals have been measured in the principal and diffuse series.[25-28] Kratz[25] resolved the *p*-doublets as far as $n = 17$, and found that they obeyed closely the law $\Delta\nu \propto 1/n^{*3}$ where n^* is the effective principal quantum number. The ^2D splitting was measured interferometrically for $n = 5$ to $n = 8$,[28] and the values are given in Table I, together with those for the first few members of the principal series. The negative sign indicates that the ^2D terms are inverted, which has also been found true for the ^2F terms.[28] The reason for this inversion is discussed in the sub-section dealing with calculations (see page 2001).

TABLE I.- DOUBLET SPLITTINGS IN THE SPECTRUM OF K I.

n	3	4	5	6	7	8	9	10
Δ^2P(cm.$^{-1}$)		57·72	18·76	8·41	4·48	2·70	1·74	1·20
Δ^2D(cm.$^{-1}$)	-2·33	-1·10	-0·503	-0·262	-0·158	-0·096		

The normal K I spectrum so far discussed is due to excitation of the 4*s* valence electron. In addition, Beutler and Guggenheimer[29] have observed the resonance doublet of the K I^b spectrum which arises from the excitation of an electron from the $3p^6$ shell.

Forbidden lines of the 4*s* – *nd* series have been found in both emission[5,30-32,45] and absorption,[31,33] and recently measured in absorption as far as $n = 13$.[34] Measured intensities have been found to agree with those expected for quadrupole transitions.[35-39] Measurements have also been made on the first members of the 4*p* – *np* series.[40,41] The appearance of forbidden lines of both the *s* – *d* and *s* – *s* series in strong external electric fields is discussed under Stark Effect. Two general reviews of forbidden lines contain references to the potassium spectrum.[42,43]

Continuous emission (recombination) spectra in potassium have been observed in several different sources.[41,46-49] The continuous absorption (photoionization) spectrum has also been investigated.[44,45,50,51] Ditchburn *et al.*[52] have summarized continuous absorption results for all the alkali metals: the curve of atomic absorption coefficient against frequency shows a characteristic minimum which for potassium lies about 0·23 eV. below the series limit. References to theoretical calculations of continuous absorption coefficients are given in the sub-section on calculations.

Theoretical calculations of line transition probabilities are also considered later (see page 2001). A full account of the methods and results of their experimental determination up to 1933 has been given by Mitchell and Zemansky,[54] and more recent work is referred to in Unsöld's book.[55] The lifetime of some excited P-states has been measured directly,[56,80] and transition probabilities of some members of the principal, sharp and diffuse series have been determined from their emission intensities in flames and arcs.[57-60] Both absolute[61,62] and relative[63-65] determinations of transition probabilities in the principal series have been made by the method of anomalous dispersion and in the sharp and diffuse series by the related 'hook' method.[66] Absolute values for the resonance lines have been found by magnetic rotation methods,[67-69] and relative values for the first twelve lines of the principal series from absorption measurements.[70] The latest results for the resonance lines (null method of magnetic rotation) give *f*-values of 0·330 and 0·657 for the $4^2S_{1/2}-4^2P_{1/2}$ and $4^2S_{1/2}-4^2P_{3/2}$ lines, respectively, corresponding to a lifetime for the 4^2P state of $2·71 \pm 0·09 \times 10^{-8}$ sec.[69] These values are about 110 times those for the second member of the principal series.[61-64]

Most of the methods mentioned above have also been used to determine the intensity ratio of the doublet members,[62,63,71-76] which is found to depart slightly from the theoretical value of 2:1, particularly at high concentrations. Theoretical explanations of this have been suggested.[77-79]

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The Spectrum of Ionized Potassium

Singly Ionized.

Lines of the K II spectrum were early found in several different kinds of source, for example discharge tubes,[4] electrodeless discharges,[5-8] certain combustion and collision processes[9-11] and interrupted arcs;[12,13] and the excitation conditions were studied in various forms of spark and condensed discharge.[14-18] Electrodeless discharges have been largely used in systematic investigations of the spectrum.[19,23,27,28,30] Much work has been done on the classification of the lines, with particular reference to the relation between the spectra of ionized potassium and neutral argon.[19-32] The wave-lengths and intensities of a few of the multiplets are given in Moore's multiplet tables.[2,3] The most recent work of de Bruin[28-30] and Bowen[32] established altogether 20 levels, which are listed in the National Bureau of Standards 'Atomic Energy Levels'.[1]

K II has an argon-like spectrum, with the ground-state electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ {}^1S_0$. Its ionization potential is 31·81 V., corresponding to a series limit of 256,637 cm.$^{-1}$ to the ${}^2P_{3/2}$ ground term of K III; the series limit to the ${}^2P_{1/2}$ term is 258,803 cm.$^{-1}$. 'Atomic Energy Levels'[1] lists terms arising from the configurations $3p^5\ 4,5s$; $3p^5\ 4p$; and $3p^5\ 3,4d$, built on both the $3p^5\ {}^2P_{3/2}$ and $3p^5\ {}^2P_{1/2}$ terms of the ion.

Doubly Ionized.

The spectra of K III and higher ions lie mostly in the vacuum ultra-violet region. A few lines of K III are included in Moore's multiplet tables.[2,3] About

80 lines in all have been classified by different investigators between 325 A. and 3885 A.,[32-38] and the nineteen energy levels derived from these are given in the National Bureau of Standards 'Atomic Energy Levels',[1] in which terms are listed arising from the configurations $3s\ 3p^6$; $3s^2\ 3p^4\ 4,5s$; $3s^2\ 3p^4\ 4p$; and $3s^2\ 3p^4\ 3d$. Since the spectrum is chlorine-like (ground state $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5\ {}^2P_{3/2}$), the terms are doublets and quartets. 'Atomic Energy Levels'[1] gives 46 V. for the ionization potential, corresponding to a series limit of 369,000 cm.$^{-1}$; a later calculation gives 46·1 V.[50]

Triply Ionized.

K IV has a sulphur-like spectrum, with the ground state $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4\ {}^3P_2$. 'Atomic Energy Levels'[1] gives 60·90 V. for the ionization potential (491,300 cm.$^{-1}$), but a more recent calculation gives 61·3 V.[50] The above tables list the nineteen levels derived from nearly 60 lines between 271 A. and 754 A. classified by Bowen[39] and Tzien,[38] with a few additions and corrections from other papers.[32,35,41-43] These terms are singlets and triplets arising from the configurations $3s^2\ 3p^4$; $3s\ 3p^5$; $3s^2\ 3p^3\ 4s, 5s, 3d$.

More Highly Ionized.

The data for K V – XI given in 'Atomic Energy Levels'[1] are indicated in Table II. The references given in parentheses are either incorporated in the main references or merely make corrections or small additions to the latter. In the 'Ionization Potential' column the unstarred values are those given in 'Atomic Energy Levels',[1] generally calculated by extrapolating the quantum defect along iso-electronic sequences by the method of Edlén.[36] Recently Finkelnburg[50] has calculated new values by extrapolating in addition the change in quantum defect down the appropriate column of the periodic table, and his values are shown starred in Table II.

TABLE II.- DATA FOR THE SPECTRA OF THE IONS K V TO K XV.

Spectrum	Iso-electronic with	Ionization Potential (volts)	Series Limit (cm.$^{-1}$)	Ground State $1s^2\ 2s^2$ +	No. of Class. lines	Wave-length Range (A.)	Refs.
K V	P I	– 82·5*	–	$2p^6\ 3s^2\ 3p^3\ {}^4S_{3/2}$	72	294–825	38 (35,39)
VI	Si I	99·7 99·88*	804,513	$2p^6\ 3s^2\ 3p^2\ {}^3P_0$	27	256–725	40 (43)
VII	Al I	118 118·24*	950,200	$2p^6\ 3s^2\ 3p\ {}^2P_{1/2}$	30	175–671	40, 44
VIII	Mg I	155 154·6*	1,247,000	$2p^6\ 3s^2\ {}^1S_0$	26	155–938	38, 45 (40)
IX	Na I	175·94 175·8*	1,419,425	$2p^6\ 3s\ {}^2S_{1/2}$	25	112–636	46(38,40,47)
X	Ne I	503·8 504·1*	4,064,300	$2p^6\ {}^1S_0$	11	29–41	48
XI	F I	– 566·2*	–	$2p^5\ {}^2P_{3/2}$	8	32–37	48 (49)
XII		630·2*					
XIII		717·7*					
XIV		789·9*					
XV		861·4*					

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The Zeeman and Stark Effects

Zeeman Effect.

The Zeeman effect in the alkali-metal doublets is described in text-books on spectroscopy, for example those cited in the Introduction. Rather fuller accounts have been given by Back and Landé.[1,2] As the historical resumés in

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the above references indicate, the 'anomalous' Zeeman pattern of the resonance lines of the alkali metals played an important part in the development of spectroscopic theory.

The Landé *g*-factor is 2 for the $^2S_{1/2}$ ground state of potassium, and 2/3, 4/3 for the $^2P_{1/2}$, $^2P_{3/2}$ levels, respectively. Thus, in terms of the classical Lorentz splitting $\Delta\nu_L$, the $^2S_{1/2}$–$^2P_{1/2}$ line has two σ components at $\pm\frac{4}{3}\Delta\nu_L$ and two π components at $\pm\frac{2}{3}\Delta\nu_L$, while the $^2S_{1/2}$–$^2P_{3/2}$ line has four σ components at $\pm\frac{2}{3}\Delta\nu_L$, $\pm\frac{5}{3}\Delta\nu$ and two π components at $\pm\frac{1}{3}\Delta\nu_L$. The Paschen–Back effect sets in at magnetic fields strong enough to break down the spin-orbit coupling; as this condition is approached, the components of the two resonance lines merge to form a Lorentz triplet with unshifted π component and σ components at $\pm\Delta\nu_L$. In addition to the references already cited, a mathematical treatment based on Dirac's theory has been given of the Zeeman effect in the alkali metals.[3]

The Zeeman effect in the ground state of potassium has been much studied in the course of atomic beam magnetic resonance experiments (see page 1999). The ground-state splittings have been measured with great accuracy in connection with a determination of the *g*-value of the electron. The $g(^2S_{1/2})$ value of potassium is found to differ from those of lithium and sodium by 1:40,000[30] and from that of hydrogen by either 1:6,000[31] or 1:60,000.[32] These small discrepancies have been ascribed to perturbations.[29]

The magnetic double refraction of potassium vapour has been measured, and experimental and theoretical results compared.[4] It has been shown from the Zeeman patterns of the 'forbidden' $4s - nd$ series of lines that they are due to quadrupole radiation.[5-7] The Zeeman effect in the $4s - ns$ series induced by an electric field has been examined.[7,8] Forbidden components have been found in the Zeeman pattern of the resonance lines[8-10,27] and a pressure-dependent asymmetry noted.[27,28] The Zeeman pattern of certain lines of the K II spectrum indicates irregularities which have been ascribed to perturbations by neighbouring configurations.[11]

The simple Zeeman pattern in any field is symmetric about the field-free line. However, at high fields and for the higher members of a series, the pattern as a whole may be asymmetrically shifted by the so-called quadratic Zeeman effect. A brief account of this has been given by White[12] with reference to the work done on potassium. The σ components should preserve their relative separation, while their centre of gravity is shifted twice as far as that of the π components, the shift being proportional to H^2 and $(n^*)^4$, where n^* is the effective quantum number. Experiments on the principal series in absorption have confirmed this up to about $n^* = 20$,[13,14] small deviations in higher terms being ascribed to perturbation of the ^2P levels by nearby ^2F levels.[13,15]

Stark Effect.

The Stark effect is rather briefly discussed in most text-books (see page 1989). A fuller account has been given by Minkowski.[16] The Stark pattern of a line is considerably more complicated than its Zeeman pattern. In the alkalies the first-order effect is an asymmetrical splitting proportional to the square of the field strength, which, when unresolved, appears as a simultaneous broadening and shift of the line. The theory of the effect in the alkalies has been discussed in several papers.[17-19]

The Stark effect has been observed in absorption in potassium for lines of the principal series and the forbidden $4s - nd$ and $4s - ns$ series;[20-24] the higher series members appear to vanish at high fields.[21,22] Calculations of line intensities for these conditions are in fair agreement with the experimental results.[25,26]

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Hyperfine Structure and Nuclear Moments

Before the development of magnetic resonance techniques, nuclear moments were determined primarily by optical measurements of the hyperfine structure, hereafter referred to as hfs. Kopfermann[1] has given a very full account of the theory and also of the methods of both optical and radiofrequency spectroscopy. Ramsey[2] has summarized the methods of determining nuclear moments, giving tables of results up to 1952 and many references. Nuclear effects in atomic spectra[33] and the role of nuclear moments in the shell model of the nucleus have recently been reviewed.[35]

The data for potassium are summarized in Table III where references are given only for the results published since 1952 and therefore not included by Ramsey.[2]

The columns headed $\Delta\nu(4^2S_{1/2})$ refer to the total hyperfine splitting of the $4s^2S_{1/2}$ ground state, which has been measured for all isotopes much more accurately by radiofrequency methods than is possible optically.[34] The first few figures of the value have here been converted for convenience to cm.$^{-1}$. μ is the nuclear magnetic moment in nuclear magnetons and Q the nuclear electric quadrupole moment.

The nuclear magnetic moments of the two stable potassium isotopes, ^{39}K and ^{41}K, are so small that the hfs is very narrow, and the difficulties of resolving it optically are increased by the fact that the isotope shift in the resonance lines is of the same order of magnitude. Early experiments failed to

TABLE III.- NUCLEAR MOMENTS OF THE POTASSIUM ISOTOPES

	I	μ (n.m.)	Q ($\times 10^{-24}$ cm.^{2})	$\Delta\nu$ ($4^2S_{1/2}$)	
				Mc/s.	cm.$^{-1}$
^{39}K	$3/2$	+0·390873[23,24] ±0·000013	0·07[25] ±0·02 or 0·11[27] ±0·02	461·723 ± 0·010	0·0154
^{40}K	4	−1·2964[30] ±0·0004	–	1285·790[30] ± 0·007	0·0429
^{41}K	$3/2$	+0·21453[24] ±0·00003	0·09[25,28] ±0·02 or 0·13[27,28] ±0·02	254·017[29] ± 0·01	0·0085
^{42}K	2 [22]	−1·137[22] ±0·005	–	1258·9[22] ± 0·1	0·0420

detect any splitting.[3,4] The hfs of the resonance lines was partially resolved when an atomic beam was used as the light source so as to reduce the Doppler width of the lines;[5-8] and in a later experiment Jackson and Kuhn[9] succeeded in resolving the ground state hfs in both isotopes and deducing the ^{2}P hfs from the unresolved structure. Their values are as follows (the $^2S_{1/2}$ values agreeing with the more accurate value quoted in Table III):-

$$^{39}\text{K}\left\{\begin{array}{l}\Delta\nu(4^2S_{1/2}) = 0{\cdot}0153 \text{ cm.}^{-1}\\ \Delta\nu(4^2P_{1/2}) = 0{\cdot}0018 \text{ cm.}^{-1}\end{array}\right. \qquad ^{40}\text{K}\left\{\begin{array}{l}\Delta\nu(4^2S_{1/2}) = 0{\cdot}0086 \text{ cm.}^{-1}\\ \Delta\nu(4^2P_{1/2}) = 0{\cdot}0010 \text{ cm.}^{-1}\end{array}\right.$$

The hfs of the Zeeman effect was also resolved, and the isotope shift[1,33] for ^{41}K relative to ^{39}K found to be +0·0076 cm.$^{-1}$.[9]

Optical spectroscopic work on hfs[10] and hfs of the Zeeman effect[11] in the alkalies has been reviewed.

The most accurate measurements of nuclear moments and of the hfs and Zeeman levels of the ground state have been made by radiofrequency methods, mainly in atomic and molecular beams.[1,2,34] Atomic beam deflection measurements[12] and the method of zero moments[13,14] were early applied to find the spins and magnetic moments of both ^{39}K and ^{41}K. Later, Rabi's magnetic resonance technique[1,2] was applied to atomic beams of potassium to measure accurately the hfs and Zeeman effect in the ground state of both these isotopes[15,16] and to molecular beams to measure directly their magnetic moments.[18,19] The g_J-value of the $^2S_{1/2}$ state of ^{39}K has been compared with great accuracy with the corresponding g_J in the other alkalies[16] and in hydrogen[17] as a step in the determination of the gyromagnetic ratio of the electron.[34]

Magnetic resonance measurements have been made on atomic and molecular beams of the radioactive isotope ^{40}K to determine its spin, magnetic moment and $\Delta\nu(4^2S_{1/2})$ value.[20,21,30] Recently the spin and $\Delta\nu(4^2S_{1/2})$ value of radioactive ^{42}K have been measured in an atomic beam, and the magnetic moment calculated therefrom.[22]

Another branch of radiofrequency spectroscopy, that of nuclear magnetic resonance,[2] has also been used to measure accurately the nuclear magnetic moments of ^{39}K and ^{41}K.[23,24]

Recently Rabi *et al.* have succeeded in performing atomic beam magnetic resonance experiments with alkali-metal atoms in excited ^{2}P states, and from transitions between hf levels of the $4^2P_{3/2}$ state of ^{39}K have found a value for the nuclear quadrupole moment of 0·07 × 10^{-24} cm.^{2}.[25] In addition, the hfs of the $5^2P_{3/2}$ and $5^2P_{1/2}$ states has been investigated by the very recent technique of magnetic double resonance, whereby radiofrequency transitions between hf levels are detected optically. The value of Q found from the $5^2P_{3/2}$ state is 0·11 × 10^{-24} cm.^{2}.[26,27] These results, combined with a molecular beam electric resonance measurement of the ratio of quadrupole moments in ^{39}K and ^{41}K give[28] a value of Q for ^{41}K of 0·09 to 0·13 × 10^{-24} cm.^{2}

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The so-called hfs anomaly[1,33,34] has been measured for the pairs of potassium isotopes ^{39}K:^{41}K[29] and ^{39}K:^{40}K[30] and found to be −0·226%[29] and −0·466%[30] respectively. The anomaly was attributed by Bohr and Weisskopf[31,32] to the distribution of the magnetic moment over a finite nuclear volume, and its size thus depends on the nuclear model chosen. The effect to be expected from different nuclear models has been compared with the experimental values.[30,32]

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Calculations

Estimates of energy levels of the potassium atom have been made from the simple Bohr theory[1] and from semi-empirical formulæ.[2,3] The behaviour of the energy levels along the iso-electronic sequence beginning with K I has been much studied (see page 1992) in many cases with reference to doublet splitting as well. Semi-empirical formulæ have also been applied to this.[4-6]

The determination of atomic energy levels and eigenfunctions (and hence transition probabilities) by the methods of quantum mechanics has been fully described by Condon and Shortley.[7] Hartree in 1946 summarized calculations carried out up to that date on the spectra of all light and a few heavy atoms for states of ionization up to the fourth.[8]

Wave functions for the ground state of potassium have been found by the

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Hartree self-consistent field method;[9] for the ground and a few excited states by an analytic treatment of the self-consistent field;[10,11] and by taking into account as well polarization of the core electrons.[12,13,35] For K^+, self-consistent field wave-functions were calculated by Hartree, first without[14] and later with[15] exchange terms, and analytic approximations have also been given.[16] Wave functions have been found for K^-,[17] and the electron affinity has been calculated by different methods; the positive value found indicates that the negative ion should be stable.[17,18,38] Wave functions for states of ionization higher than the first appear to have been calculated only for the ground states of the ions K XII[40] and K XIV.[39]

Several explanations have been given of the inversion of the ^2D and ^2F terms of the heavier alkalies:[19-23] it is generally ascribed to perturbations by excited states of the core electrons. The ^2P intervals have been calculated from Hartree wave functions.[24]

Transition probabilities have been calculated on the basis of Hartree self-consistent field wave functions for members of the principal, sharp and diffuse series,[12,13,25-27,34] and also for the 'forbidden' 4*s* – *nd* series.[28,29] Several calculations of continuous absorption coefficients (photo-ionization cross-sections) have been made,[30-33] of which the most recent,[31,33] using wave functions with exchange, have succeeded in accounting qualitatively for the experimentally determined coefficient, including the minimum below the series limit. The continuous absorption coefficient of K II has also been calculated, with the use of exchange wave functions of K III.[37] In the *X*-ray spectrum, calculations have been made for the continua at the *K* and *L* absorption edges, using Hartree–Fock wave functions.[36]

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Pressure Effects and Fluorescence

Pressure Effects.

General accounts of the effects of pressure on spectral lines are given[1,2] in several text-books. In addition, review articles were written in 1936 by Margenau and Watson[4] and in 1957 by Ch'en and Takeo;[3] both of these contain many references to work on alkali spectra, on which some of the most extensive research has been done, and accounts of the theories of pressure effects. More detailed theoretical papers have been published on both foreign-gas broadening[5-8] and 'resonance' (self-pressure) broadening.[9,10] In view of the availability of these review articles the subject may be treated very briefly here.

Both broadening and shift have been measured in absorption for the potassium resonance lines[11-14] and the next few doublets of the principal series,[15,16] with a number of foreign gases. The doublet intensity ratio has been found to vary with pressure.[14] The shift in the higher members of the series is proportional to the relative density of the foreign gas and approaches a constant value at the series limit,[17-20] but the line width does not behave in quite the same way.[19,20]

Another effect of pressure is the appearance of bands near the absorption lines. These have been investigated in potassium vapour and attributed to the formation of loosely bound polarization molecules of K_2.[21-28]

The behaviour of the potassium resonance lines with increasing density of potassium vapour (resonance broadening) has also been investigated. Experimental line contours have been compared with calculated contours.[29-31] At high vapour pressures, asymmetries have been noted in the Zeeman pattern of the resonance lines, together with the appearance of forbidden components.[34,35]

High vapour pressures have also been found to affect absorption coefficients in both the continuous spectrum[32] and the principal series.[33]

Fluorescence and Resonance Radiation.

A full general account is given by Mitchell and Zemansky.[1] In potassium the excitation of resonance radiation has been described,[37] and experiments have been done on its polarization[36] and quenching by hydrogen and deuterium.[40] Several lines and bands have been observed in fluorescence.[38,39]

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X-Ray Spectrum

Early work on the *X*-ray spectrum of potassium was principally concerned with measurements on the *K*-series lines[1-5,8,11,13] and of the effect on the wavelength both of the *K*-emission lines[7,9,11,23] and of the *K*-absorption edge[6,10,12] of using potassium in different chemical compounds. Measurements were also made on *L*-series lines,[15,16] and the *K*-, *L*- and *M*-absorption edges calculated.[14]

With increasingly good resolution, satellites were found near many *X*-ray emission lines, including the *K*-series lines of potassium.[17-19,21,22] These appear to originate in atoms in which a second electron has been knocked out of an inner shell, either together with the first or in an Auger process.[19] The production of Auger electrons has been investigated.[38]

Other effects studied in potassium include the Compton scattering effect,[26] *X*-ray emission from gaseous potassium,[13] the existence of extremely soft *X*-ray absorption bands in the potassium atoms in photographic plate emulsions[27] and of semi-optical bands,[25] and the fluorescent yield of *X*-ray emission.[28] The mass absorption coefficient has been measured and compared with that calculated by taking into account both photoelectric absorption and scattering,[29] and the energy distribution of the ejected photoelectrons has been investigated.[24] Work on the *X*-ray spectra of potassium and other elements was reviewed in 1938.[30] Recently a table of atomic energy levels has been compiled from *X*-ray frequencies for potassium and other light and medium elements.[44]

With the higher-resolution methods developed since the early years of *X*-ray spectroscopy, it has been shown that the absorption edges of atoms in the

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solid state have a fine structure and that owing to the influence of unbound electrons and neighbouring atoms many of the emission 'lines' are in fact bands of varying widths. Much work has been done on the *K*-absorption edge of potassium, principally in halide crystals,[20,31,32,34,35,40,42] but also in aqueous solutions[41] and in metallic potassium.[36,43] The effect depends on electronic energy bands in the crystal lattice or, in the case of a metal, on the free electron conduction bands.[37,39,42,43,48] These also affect the width and shape of emission bands.[33,37,39,42] The study of *X*-ray absorption and emission bands is now a valuable part of solid-state physics.[37,39,42,43,48]

Another recent development in *X*-ray spectroscopy is the production of so-called mesonic *X*-rays – *i.e.*, *X*-rays from an atom in which the radiating electron is replaced by a meson. Information can be derived about both the meson and the atomic nucleus. In potassium, *K*-, *L*-, and *M*-series lines have been identified from π-mesonic atoms.[45–47]

A number of general accounts and review articles discuss the *X*-ray spectrum of potassium, with particular emphasis on the importance of *X*-ray spectroscopy in solid-state physics.[49–51]

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THE MOLECULAR SPECTRA OF POTASSIUM AND CERTAIN OF ITS COMPOUNDS

By R. F. BARROW

The Potassium Molecule, K_2

The small proportion of diatomic molecules, K_2, in equilibrium with K atoms in the gas phase at any temperature gives rise to a number of band systems, not all of which have yet been fully investigated. The bands may be observed most readily in absorption,[1-4,8,10,12,14] but many are also seen in the fluorescence spectrum,[2,5-7,28] and excitation by active nitrogen[11] has also been studied. Early analyses (e.g. [3,13]) were based on inadequate data; there is now little doubt that the analyses of the longer-wave-length systems[14-16] are correct, but the ultra-violet bands[19-24] are less well understood. The magnetic rotation spectrum of the system $B^1\Pi_u - X^1\Sigma_g^+$ (see Table IV) has also been examined both experimentally[16] and theoretically;[18] the observations give important information about the course of the vibrational levels in the excited state and lead to a value for the dissociation energy of the K_2 molecule. The isotope effect between the bands of $(^{39}K)_2$ and of $^{39}K^{41}K$ has been observed.[7,9] From the alternation of intensities of the rotational lines it was concluded[15,29] that the nuclear spin of ^{39}K is greater than 1/2. The relative intensities of bands in the B–X system has been studied.[30]

There is also spectroscopic evidence of weakly-bound polarization molecules.[17,25-27] Diffuse absorption bands are attributed to weakly-bound molecules K–X, with X = ^{40}Mg, ^{41}Zn, ^{41}Cd and ^{41}Hg.

The dissociation energy of K_2 may be obtained from the convergence limit in the state $B^1\Pi_u$, giving $D_0'' = 0{\cdot}514$eV. or $11{\cdot}8_5$ kg.-cal.mole^{-1}. It is, however, possible that there is a small potential maximum in this state; if so, this estimate could be a little too high. Molecular-beam experiments[16,31,32] yield in fact still higher values. A recalculation,[34] for example, of the results of Lewis,[31] gives $D_0'' = 12{\cdot}67 \pm 0{\cdot}50$ kg.-cal. Studies of dilute potassium-chlorine and potassium-bromine flames[33] give $D_0'' = 12{\cdot}5$ kg.-cal.

An accurate potential-energy function for the ground-state of K_2 has been constructed,[35] and a number of empirical relations between the spectroscopic constants of this molecule has been discussed.[36-40]

TABLE IV. - SPECTROSCOPIC CONSTANTS FOR K_2

State	T_0	ω_e	$x_e\omega_e$	$y_e\omega_e$	B_e	α_e	r_e, A.
G	28077	64·9	$0{\cdot}5_5$	-	-	-	-
F	27556	62·3	$0{\cdot}2_4$	-	-	-	-
E(1)	26480	$63{\cdot}0_9$	0·4	-	-	-	-
$D(^1\Pi_u)$	24611·0	61·60	0·9	+0·001(2)	-	-	-
$C(^1\Sigma_u^+)$	22954·0	60·60	0·2	-	-	-	-
$B^1\Pi_u$	15369·2	75·00	0·3876	+0·004366(3)	0·04824	$2{\cdot}35 \times 10^{-4}$	4·235
$A^1\Sigma_u^+$	11670·9	69·09	0·153	-	-	-	-
$X^1\Sigma_g^+$	0	92·64	0·354	-	0·05622	$2{\cdot}19 \times 10^{-4}$	3·923

Notes (1) Slightly different constants are given in reference 24.
(2) $-0{\cdot}0003(v + \frac{1}{2})^4$.
(3) $-0{\cdot}00018(v + \frac{1}{2})^4$.
(4) No satisfactory analysis has yet been proposed for the bands[24] in the region 3420 to 3640A.

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KRb, KCs

Diffuse absorption bands at 20,160 and 18,560 cm.$^{-1}$ have been attributed to the molecules KRb and KCs respectively.[1]

Reference

1 Walter, J. M. & Barratt, S., *Proc. Roy. Soc.*, 1928,**A119**,257-75. (*22*,2885)

Potassium Hydride

The spectrum of potassium hydride[1-3] is similar to the spectra of the other alkali-metal hydrides. An emission continuum has also been observed.[4] Analyses of bands of the A–X system[5,6] appear to be incorrect.[7] Constants for KH are given below. For a general discussion of the alkali-hydride spectra, see reference 8 and LiH, page 285.

State	T_e	ω_e	$x_e\,\omega_e$	D_0, kg.-cal.
$A^1\Sigma^+$	19530·2	251·0	−4·5*	–
$X^1\Sigma^+$	0	985·0	14·65	$42\cdot_9$

continued on following page

State	B_e	α_e	r_e, A.
$A^1\Sigma^+$	1·32	-0·04*	$3{\cdot}6_1$
$X^1\Sigma^+$	3·407	0·0673	2·244

* Further terms are required to describe the variation of G and of B with v in $A^1\Sigma^+$.

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Potassium Halides

The spectra of the potassium halides in absorption in the vapour state have been investigated as follows:-

Microwave region: potassium chloride[1] and iodide.[1]
Infra-red (vibration-rotation) region: potassium chloride[2] and bromide.[2]
Electronic spectra: potassium fluoride,[3,4] chloride,[3,5,7] bromide[3,5-7] and iodide[3,5-7]

The electronic spectra of the chloride, bromide and iodide have also been studied in emission.[7] Information about the spectroscopic properties of potassium fluoride has also been obtained by the molecular beam electric resonance technique.[8] In an important development of this method, accurate molecular constants for potassium chloride[12] and bromide[13] have been derived from observations of lines of the transition J = 0 → J = 1. Measurement of the Stark pattern of the line J = 2 → J = 3 in potassium chloride leads to the value μ = 10·1 ± 0·2D. for the dipole moment. Radio-frequency spectra have also been observed for potassium fluoride[15] and bromide.[16]

Values of the molecular constants of these molecules are collected in Table V, together with the thermochemical information required for the determination of their energies of dissociation (see also page 283).

TABLE V. - SPECTROSCOPIC CONSTANTS FOR THE GASEOUS POTASSIUM HALIDES

Molecule	B_e	α_e	r_e, A.	ω_e, cm.$^{-1}$	μ, D.
KF	-	-	[2·129]	~400$^{(4)}$	8·62
KCl	3856·40$^{(2)}$	23·680$^{(2)}$	2·6666	281	10·48
KBr	2434·95$^{(3)}$	12·136$^{(3)}$	2·8207	213	10·41
KI	1825·01	8·034	3·0478	[173]	11·05

Notes: (1) The values of B_e, α_e and r_e are taken from reference 1. The values of B_e and α_e are in Mc./sec.
(2) Constants for $K^{35}Cl$.
(3) Constants for $K^{37}Cl$.
(4) ω_e(KF) ~405cm.$^{-1}$ from ultraviolet spectrum,[4] 390 ± 40cm.$^{-1}$ from molecular beam electric resonance.[8] Other values of ω_e are from reference 2: the values in square brackets are estimated values.

continued on following page

TABLE V (continued)

Dissociation Energies, D_{298}, kg.-cal.mole^{-1}				
	KF	KCl	KBr	KI
$-Q_f$(MX)	134·46[a]	104·175[a]	93·73[a]	78·31[a]
$-\Delta_s H$(MX)	-57·8[b]	-52·88[b]	-50·5[d]	-48·0[d]
$\Delta_s H$(M)	21·49[c]	21·49[c]	21·49[c]	21·49[c]
Q_f(X)	18·86[d]	29·01[a]	26·71[a]	25·48[a]
D_{298}	117·1	101·8$_0$	91·4	77·3

a reference 9
b reference 10
c reference 11
d recalculated from reference 17

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POTASSIUM AND POTASSIUM COMPOUNDS: SOLID STATE

Potassium

Films of potassium deposited on fluorite at liquid air temperatures are transparent in the Schumann region[1] (see also page 1378).

Reference

1 Watson, W. H. & Hurst, D. G., *Canad. J. Res.*, 1936,**A14**,153-7. (*30*,7456)

Potassium Hydride

The ultra-violet absorption of thin crystalline layers of potassium hydride deposited on quartz has been measured.[1] Absorption maxima are found at 2350 and 1930 A.

Reference

1 Rauch, W., *Z. Phys.*, 1939,**111**,650-6. (*33*,6155)

Potassium Oxides

The ultra-violet absorption of thin layers of the monoxide, K_2O, deposited on quartz has been measured.[1] Absorption maxima are found at 3120, 2550 and 2290 A.

The infra-red absorption spectrum of a sample presumed to be potassium trioxide, K_2O_3, has been examined,[2] but no absorption attributable to the ion $O_3^=$ was observed.

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Potassium Halides

In order to avoid repetition, certain properties of the crystalline alkali metal halides are only discussed in detail under one appropriate alkali metal, as follows: ultra-violet absorption spectra, page 285; Raman spectra, page 1380; colour centres, page 2012; luminescence: phosphors, page 2018.

The absorption spectra have been studied in both the infra-red and ultra-violet regions. In the infra-red, maxima have been observed[1] as follows:-

KCl: 70·7μ. KBr: 88·3μ. KI: 102·0μ.

In the ultra-violet region, the maxima[2-5,24] lie at the following wave-lengths:-

KF: 1260 A.
KCl: 1620 1310 A.
KBr: 1870 1730 1460 A.
KI: 2190 1870 1750 1290 A.

The variation with temperature of the position of the longest-wave-length absorption band of potassium iodide has been studied.[6] On melting, the ultra-violet absorption edges shift by about 0·7eV. to longer wave-lengths.[7,8] Other measurements of the dispersion of potassium chloride in the ultra-violet region,[9] and of the ultra-violet reflexion spectrum[10] have been reported. The refractivity of potassium bromide in the visible region, $4000 \leqslant \lambda \leqslant 7100$ A., at temperatures between 16° and 28° C. has been measured.[11] Absorption by potassium chloride in the microwave region has been discussed in terms of lattice defects.[23]

In the infra-red region, natural potassium chloride was once important as a prism material; measurements of its refractivity[12] and transmission[13] are available. More important[14] is potassium bromide, especially for the region 15 to 25μ. The refractivity[15,16] of potassium bromide, and its transmission[13,17] have been studied. The transmission of powder films has also been measured,[18] and its use in filters for the region 30 to 43μ has been discussed.[19] Potassium iodide is little used in infra-red spectroscopy: its refractivity[16] and transmission[20] have been measured.

The use of the potassium halides, alone, or with controlled additions of thallium or lead, as filters transmitting narrow intervals in the ultra-violet region has been discussed,[21] as has the use of potassium chloride–lead chloride and potassium bromide–lead bromide.[22]

Refs. p. 2011

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Potassium Halides and Infra-red Spectra of Solids

In an important technique[1] for the examination of the infra-red absorption spectra of solid substances, the powdered material is incorporated in a sintered disk commonly of potassium bromide (technique,[1-10] applications[11-16]). The chloride[17] and iodide[3,18] may also be used.

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Raman Spectra

The Raman spectra of the potassium halides have been studied in some detail, both experimentally[1-6] and theoretically.[7-10] Infra-red absorption frequencies have also been measured.[11] For a review of the Raman effect in solids and a discussion of the vibrational spectra of the alkali halides, see Menzies[12] (see also page 1380).

A study[13] of the Raman effect provides no evidence for the existence of undissociated molecules in aqueous solutions of potassium chloride at concentrations up to 4N. Fine structure in the nuclear paramagnetic resonance absorption line for protons in $KF,2H_2O$ has been studied.[19]

The infra-red spectra of crystals of KHF_2 and of KDF_2 have been examined[14-18] with the object of elucidating the structure of the bifluoride ion (Mellor, Suppl. 2, Part 1, 234), now known to be symmetrical.

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Colour Centres

Coloured crystals of the alkali halides may be formed in two distinct ways: (i) by subjecting the crystal to ionizing radiation (e.g. γ-rays, neutrons, X-rays, ultra-violet light), (ii) by the introduction of a stoicheiometric excess of alkali metal, achieved by heating the salt in the metal vapour. The coloration arises from a wide bell-shaped absorption band, the *F*-band,[1-6] in the region 4000 to 8000A., which appears to constitute a single transition, broadened by interactions with the lattice vibrations. There is, however, a shoulder and tail on the low-wave-length side of the *F*-band, called the *K*-band.[101] This appears to be intimately connected[5] with the *F*-band (see, however, [102-104]). The coloration of the alkali halides was first studied by Pohl and his collaborators;[1,2] the subject proves to be of great interest in connexion with the study of the imperfections of the crystal lattice, and has attained growing attention (for reviews, see [1-6]).

De Boer[12] first suggested that the *F*-centres[7-47] (Farbzentren) responsible for the absorption are electrons trapped at a halogen-ion vacancy, thus:-

$$\begin{array}{ccccc} + & - & + & - & + \\ - & + & \boxed{\bullet} & + & - \\ + & - & + & - & + \end{array} \qquad F\text{-centre}$$

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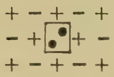
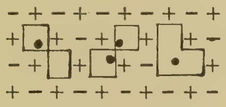
This view has been amply confirmed by later work: it may be noted, for example, that in additively coloured halides, (i) the colours are independent of the alkali metal used in coloration, and (ii) the number of F-centres, measured optically, proves to be equal, so far as can be determined, to the stoicheiometric excess of alkali metal.[11] Concentrations as high as 10^{19} centres per c.c. can be produced.

If cooled crystals containing F-centres are illuminated with light falling within the F-band, the number of F-centres decreases, so that the F-band is bleached, and at sufficiently low temperatures a new broad absorption band is formed at longer wave-lengths than the F-band, the F'-band. At the same time, the crystals become conducting.[73-91] Measurement of the photo-current as a function of the incident light intensity leads to a determination of the mean distance which the electron travels before it is trapped. It turns out that this path-length is inversely proportional to the concentration of F-centres, so that the trapping centres are the F-centres themselves. The F'-centres are therefore considered to consist of two electrons trapped by an anion vacancy:-



F'-centre

Irradiation of coloured crystals within the F-band at room temperature and above leads to coagulation of the F-centres. Anion vacancies, formed by ionization of F-centres, join with cation vacancies to form pairs which are capable of rapid diffusion. In the initial stages of coagulation, R_1, R_2, M and N bands are observed in absorption.[124-132] The centres may be represented as follows:-



R_1 R_2 M

The end result of the coagulation process in additively coloured crystals is the production of colloidal aggregates[110-123] of F-centres, indistinguishable from colloidal particles of alkali metal.

Alkali halides containing F-centres show spin resonance absorption lines[61-72b] associated with the unpaired electrons in the F-centres. Study of (i) the g-factor, which determines the splitting of energy levels per unit magnetic field, and of (ii) the breadth of the absorption lines, shows that the electrons are not completely 'free'. Seitz[5] concludes that 'the electrons in the F-centres belong to the ions of the lattice in a very real way and are not confined entirely to the vacant lattice space. The interaction between the electron and the ions is sufficient to preclude the electron being treated exactly as if it moved in a central field' (see also [46-60]).

Additively coloured crystals of potassium chloride, bromide and iodide and of rubidium chloride have also been shown to possess a sharp absorption band, the β-band, lying just towards the long wave-lengths of the fundamental ultraviolet absorption band.[105-109] This β-band is closely associated with the F-band. If the crystal is irradiated in the F-band so that F' centres are formed, the β-band is also bleached and a new band, the α-band, appears at longer wave-lengths than the original β-band, but still close to the fundamental. On decomposing the F'-centres by warming, the β-band is regenerated along with the F-band. There is evidence that the α-band is associated with the transition of an electron from a halogen ion to an excited state near an anion

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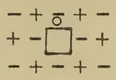
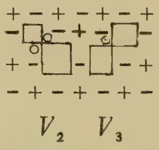
vacancy, while the β-band is believed to arise by transition to an excited state near an F-centre.

Crystals coloured by ionizing radiation exhibit ultra-violet absorption bands, V-bands,[133-152] not shown by the additively coloured halides. In coloration, electrons are transferred from the full band to anion vacancies, leaving a positive hole in the full electron band. This would be expected to be trapped at cation vacancies to give an absorbing centre, the V-centre, such as should also be found on treating crystals with an excess of halogen. Indeed, potassium bromide treated with bromine is found to possess V-bands. The centre may be represented thus:-



as a hole plus a cation vacancy. Other bands, V_2, V_3, vary in intensity with the first power of the halogen pressure, and are thus associated with centres containing pairs of positive ion vacancies:-



On colouring at liquid helium or liquid nitrogen temperatures, the V_1 band, if it occurs, is masked by a strong band H.[153,154] H-centres may be holes trapped at neutral vacancy pairs.

For a photographic application, see [155].

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H Band.

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Colour Centres in Mixed Crystals

F-bands and other absorption bands have also been studied in the following systems: mixed crystals of potassium chloride-bromide,[1,2] potassium-rubidium chloride,[1,2] sodium-potassium chloride,[2] sodium chloride-bromide[2] and potassium bromide-rubidium chloride;[2] sodium chloride-(silver),[3-5] sodium bromide-(silver),[3,4] potassium chloride-(silver),[4] potassium bromide-(silver),[4] sodium bromide-(iodide),[6] potassium bromide-(iodide),[6] sodium chloride-(nitrite),[7] sodium bromide-(nitrite),[7] potassium chloride-(nitrite),[7] potassium bromide-(nitrite),[7] potassium bromide-(nitrate),[8] potassium chloride-(cadmium),[9] sodium chloride-(calcium),[10] sodium chloride-(cadmium).[10]

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Addition of Hydrogen

Another absorption band, the *U*-band, appears relatively far in the ultraviolet region when the hydride of a given alkali metal is added to the corresponding halide. The *U*-centre appears to consist of a negatively charged hydrogen ion, H^-, occupying substitutionally the position of a halogen ion.

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Luminescence

Crystals of the alkali halides have been found to luminesce under a variety of conditions, even when the substances have been supposed to be pure. Luminescence is for example observed when crystals are bombarded by particles, such as α-particles[3,12] or electrons,[14] or are subjected to the action of *X*-rays[1,5,7,10,11] or γ-rays.[12] However, very small amounts of impurities have a drastic effect upon the properties of these substances;[2] for example, as little as 4 parts of copper in 10^8 of sodium chloride stimulates measurable luminescence.[17] It is therefore doubtful if all the reputedly 'pure' materials which have been studied have been adequately freed from impurity-ion activators. A pure crystal, with no more than the normal concentrations of lattice defects, has presumably no detectable luminescent properties; but the attack of sufficiently energetic particles or photons may create sufficient lattice disturbances to lead to measurable luminescence, and a number of observations have been made of the luminescence of crystals containing colour centres.[4,6,9] Thermoluminescence[16,19] may also be observed, as for example on heating crystals which have been irradiated with *X*-rays at a low temperature.

A complete interpretation of these phenomena remains to be found: even in the case of what might be expected to be one of the more simple problems, that of the luminescence of *F*-centres themselves, there is marked disagreement between present theory and experiment. The former[13,13a] predicts *F*-centre fluorescence with high efficiency at long wave-lengths (~10,000A. for potassium chloride), while one set of experiments has been negative;[17] latterly what appears to be the predicted fluorescence has been observed,[18] but with an efficiency of not more than about 1%.

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The results of experiments on the thermoluminescence of X-ray treated sodium chloride[20] are also difficult to understand. They suggest that there is a two-stage process in which the first stage is, by thermal activation, the elevation of trapped electrons from F-centres into the conduction band. In the second stage, electrons in the conduction band fall back into empty levels, of which at least five have been recognized, with widely differing probabilities.[20]

The degree of polarization of luminescent radiation has also been investigated.[15,21] Luminescence has also been observed in crystallization from saturated solutions on addition of hydrochloric acid or on rapid cooling.[8]

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Activated Potassium Halides

Large single crystals of the alkali halides may be prepared containing small amounts of an added foreign metal; in one instance at least, that of potassium chloride to which small amounts of thallium have been added, there is a random replacement of potassium ions by thallous ions throughout the lattice, and the optical phenomena are comparatively simple and are now well understood.[1-6]

In the ultra-violet region, the presence of a foreign ion commonly leads to the appearance of a new absorption band, lying to longer wave-lengths than the fundamental absorption band of the pure halide.[7,8] Measurement of the intensity of the ultra-violet absorption band leads to a determination of the number of dispersion electrons, and in potassium (thallium) chloride, this number proves to be equal to the number of thallous ions determined analytically[21,30] (the analysis must be done on the crystal for the concentration of thallium is less in the crystal than in the melt from which it is grown[20]). Thus, the thallous ions are dispersed randomly throughout the crystal. A second observation is that the ultra-violet absorption spectra of these impurity centres

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are commonly similar to those of the analogous concentrated aqueous solutions.[13,14,19,24] The variation with temperature of the absorption spectra of activated crystals has been studied,[10,12,15,16,25-27] as has the effect of treating the crystals with *X*-rays.[18,29] Among a number of activators, the action of the following has been investigated: thallium,[8,10,11,14,16-21,24-27,30] lead,[8,10,11,14,16,18-20] copper,[9,12,13,15,28] silver,[9,13,16,28] nickel,[22,23] tin,[29] thorium.[28]

On the colours of natural rock salts, see [31,32].

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Activated Halides: Luminescence and Phosphorescence

Luminescence may be observed in alkali halide crystals containing small amounts of activating ions,[1] such as thallium,[3,4,6-8,10,11,13-15,19,21,22,24,26-33] silver,[12,20,23,25,27,34,35] copper,[4,12,17,18] nickel,[9,17,18] manganese[2,12] and lead.[4,12] Apparently the halides may also be activated by polysulphides.[16] Luminescence is observed not only in the crystals, but also in concentrated aqueous solutions.[11] The phosphors are not photoconductors:[28] however, electron emission in sodium (silver 1·5%) chloride has been observed after excitation by *X*-rays.[34] Luminescence is often excited by light of appropriate wave-length, but it may also be stimulated by *X*-rays, γ-rays, α-particles, protons and other particles. If energy is absorbed, for example by irradiation at a low temperature, it may be stored in the crystal as a defect of some kind, e.g. *F*-centres, and thermoluminescence may be observed on raising the temperature as the defect

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acquires sufficient thermal energy to escape from its trap. The analysis of glow curves, *i.e.* thermoluminescence curves for steadily rising temperature, thus gives important information about crystal energy levels:[13,17-20,29,31,32] studies of the variation of luminescence intensity with time[3,7,9,12,13,18,19,21-25] and with wave-length of incident stimulating light[10,27,33] are also of importance. On the luminescence of natural rock salts, see [46].

Potassium chloride phosphors containing small amounts (~0·01%) of thallium have been examined in great detail, and their main properties are now elucidated (see reference 6, page , and [39-44]: for further theoretical discussion, see also [13,36-38]). The ground state of the thallous ion, Tl^+, is $6s^2\ {}^1S_0$. The lowest excited states, arising from the configuration $6s6p$, are ${}^3P_0$, ${}^3P_1$, ${}^3P_2$ and ${}^1P_1$. As in mercury, the coupling is near j–j, so that the transition ${}^3P_1 \leftarrow {}^1S_0$ may be expected to appear as a not very strongly forbidden transition as well as the allowed transition ${}^1P_1 \leftarrow {}^1S_0$. The former, in potassium (thallium) chloride gives rise to an absorption band at 2490A., the latter to a band at 1960A. In the lattice, the energy levels of the thallium ion are broadened by interaction with the six surrounding chloride ions, and to a different degree and extent for the different energy states of Tl^+. The operation of the Franck–Condon principle is such that whereas the absorption ${}^3P_1 \leftarrow {}^1S_0$ lies at 2490A., the luminescence emission corresponding to the same transition has its maximum at 3050A. Similarly excitation to the ${}^1P_1$ state by absorption at 1960A. gives rise to fluorescence radiation at 4750A. If the crystal is irradiated at a low temperature, the metastable states ${}^3P_2$ and ${}^3P_0$ may become appreciably populated. Since transitions to the ground state from these excited states are forbidden, energy is stored in the crystal until sufficient thermal energy is available for a radiationless transfer from the metastable states to one or other of the excited states which can combine with the ground state. On heating the excited crystal, it is found that there are two bursts of emission, one at about 200°K., the other at about 300°K., corresponding to traps about 0·35 and 0·72eV. deep, respectively. This picture of the transitions in the potassium (thallium) chloride phosphor has been quantitatively confirmed by absolute calculations by Williams, based on the lattice energy of the crystal and the wave-functions for the thallous ion.[39-41]

In contrast, sodium (silver) and potassium (silver) chlorides show non-uniform distribution of activator.[35] The energy changes and displacements following the introduction of Mn^{2+} ions into the sodium and potassium chloride lattices have been calculated.[45]

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Scintillation Counters

Activated crystals of the alkali halides, of which sodium iodide (thallium) has proved to be one of the most important, are among the substances which luminesce on exposure to particles such as α-particles and protons or to γ-ray, X-ray or ultra-violet photons of above a minimum energy. The luminescence may be observed by a photomultiplier the output of which is amplified to give a voltage pulse following the absorption of a particle or photon by the crystal. This arrangement constitutes a *scintillation counter*, having properties as a detector of nuclear radiation, especially high sensitivity to γ-rays, rapid response time and high resolution, which render it superior for many purposes to other detectors such as the Geiger-Müller counter.[1-5]

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Potassium Sulphate

The isotope effect in the infra-red absorption spectrum of potassium sulphate

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has been noted.[1] An electronic band system shown by potassium permanganate–potassium sulphate crystals has been studied at low temperatures.[2]

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Potassium Carbonates

Infra-red powder absorption spectra have been observed for potassium bicarbonate[1] and potassium carbonate.[2]

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Potassium Nitrate

The Raman spectrum of potassium nitrate has been studied in aqueous solution,[1] in the crystal,[3] and in the fused state.[2,4] The frequencies of the nitrate ion are lower in solution than in the crystal,[1] but the frequencies of the nitrate ion in the fused salt[4] are little altered from their values in the crystal, and it is concluded that the individual ions persist unchanged in the melt. The assignment of frequencies to vibrational modes has been discussed,[3] and details have been elucidated through observations on the infra-red spectra[5,6] of samples in which 50% of the nitrogen content was ^{15}N. The Raman spectra of mixed crystals $NaNO_3$–KNO_3 have also been examined.[7]

The ultra-violet absorption[8] and reflexion[9] spectra have been studied. Enolization in solutions of potassium nitrate in acetone has been studied by observations of their infra-red spectra.[10]

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Potassium Phosphates

Infra-red powder absorption[1,2] and reflexion[3,4] spectra have been reported for a number of potassium phosphates. The Raman effect in Graham's salt has also been examined.[5] The frequency of the O–H stretching vibration in KH_2PO_4 is found[6] at 2370 cm.$^{-1}$, *i.e.* at about 1330 cm.$^{-1}$ less than the normal value, indicating strong hydrogen-bonding. The infra-red spectrum of KD_2PO_4 has also been studied.[6] An interpretation of the splitting of the O–H frequency

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observed in the Raman effect has been given.[7] The ultra-violet absorption spectra of a number of potassium phosphates have been examined.[8]

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SECTION LX

THE ANALYTICAL DETERMINATION OF POTASSIUM

By H. V. THOMPSON

DETECTION

The sensitivity of the flame test for potassium is said to be greatly increased by using as a filter an aqueous solution of chrome alum (310 g. per l.) which completely absorbs light from the alkaline earth metals, sodium and lithium, but transmits that from the other three alkali metals, the potassium flame appearing crimson.[1] Attention has been directed to the quality of the cobalt glasses commonly used in the flame test as many of them absorb the red lines which are most readily detected in a spectroscope.[2] The spectrographic limit of identification of potassium has been found to vary widely with the form in which the element is introduced,[3] and the sensitivity also depends on the mode of excitation in the ascending order spark, flame and arc.[4]

In the standard cobaltinitrite test for potassium the interference of ammonia and ammonium salts can be prevented by the prior addition of formaldehyde, whereby hexamethylenetetramine is formed,[5,6] and the test has also been modified by treating the well washed precipitate with ammonium sulphide to give cobalt sulphide.[7-9] If zinc or magnesium cobaltinitrite is used, it is then possible to test for sodium in the filtrate from the precipitated potassium salt.[10,11] Several variants of the normal reagent have also been proposed.[12-14] Reed and Withrow recommend the use of zirconium sulphate and claim that this reagent is nearly as sensitive as the cobaltinitrite test and superior thereto in that the other alkali metals, magnesium and the ammonium radical do not interfere.[15-19] Potassium forms sparingly soluble salts with a number of nitro or polynitro organic compounds, e.g. picric acid,[20-23] dipicrylamine,[24-31] Naphthol Yellow S,[32,33] 4:6-dinitrobenzofuroxan,[34,35] dilituric (5-nitrobarbituric) acid[31,36,37] and certain nitrosulphonic acids,[38,39] all of which have been suggested as suitable reagents for the detection of the element. A few papers have been published on reagents for the detection of potassium with particular reference to the sensitivity and specific nature of the tests.[40-43,405]

DETERMINATION BY CHEMICAL METHODS

Within the last twenty-five years a number of reviews have appeared on the determination of potassium by gravimetric, volumetric and physical methods, on both the macro and the micro scale.[43,44-53]

Gravimetric Methods.

The three methods most commonly used for the determination of potassium are the cobaltinitrite, the chloroplatinate and the perchlorate methods. The first of these is based on the precipitation of a complex potassium sodium cobaltinitrite which when dried to constant weight is assumed to have the composition, $K_2NaCo(NO_2)_6,H_2O$. Cæsium, rubidium and ammonium must be absent as they also form sparingly soluble cobaltinitrites, but magnesium, zinc, calcium, strontium, aluminium and iron do not interfere.[54-62] Other cobaltinitrites can replace the sodium salt.[62a,406]

Although the separation of potassium from sodium is quantitative, a considerable volume of evidence has accumulated which suggests that the composition of the precipitate is influenced by a number of factors and that reliable results can only be obtained by making a parallel determination with a known and comparable amount of potassium.[63–76] Indeed, Duval concludes as a result of thermogravimetric analysis that 'the use of this mixed complex ought to be banned from gravimetric and microgravimetric analysis (especially from its practical application to the determination of potassium in blood and urine)'.[77] On the other hand it is claimed that by careful attention to conditions of precipitation and by evaporating the mixture to a pasty mass before filtration the inherent errors in the method can be so reduced as to give satisfactory results, particularly in the field of soil analysis[78–80] and biochemical assays,[81–88] although a volumetric rather than a gravimetric finish is often preferred (see below).

In micro determinations a number of analysts recommend comparing the height or volume of the precipitate measured in a centrifuge tube with that obtained from standard solutions of potassium.[89–94]

The chloroplatinate method[95] is based on (i) the quantitative conversion of the mixed chlorides of sodium and potassium into chloroplatinates on treatment with hydrochloroplatinic acid, and (ii) the very slight solubility of potassium chloroplatinate in aqueous ethyl alcohol in which the sodium salt is readily soluble.

The concentration of the alcohol is important, however, as there is much evidence to show that high concentrations of alcohol give high results and vice versa.[96–107] In general practice alcohol of 80 to 85% strength is used. Low results have also been attributed to traces of aldehydes in the alcohol.[108,109] Conditions of precipitation likewise affect the accuracy of the determination and the concensus of opinion is that a dilute solution of the mixed chlorides, containing only a slight excess of hydrochloroplatinic acid, should be evaporated to a syrupy consistency before extraction with alcohol.[110] After filtering and washing, the precipitate is then dried to constant weight.

Lithium, sodium, magnesium, calcium and strontium do not interfere, but any rubidium or cæsium will be precipitated with the potassium. It is also essential to carry out the whole determination in an atmosphere free from ammonia to avoid the formation of ammonium chloroplatinate which, like the potassium salt, is sparingly soluble in alcohol.

In the presence of barium, aluminium and iron, the chloroplatinates of which are either soluble in or decomposed by alcohol, the impure, washed precipitate is redissolved in water, reduced, and the platinum weighed.[111–115] This modification also enables a determination to be made in the presence of borates, nitrates, phosphates or sulphates, but as a general rule it is advisable to remove all metals and acid radicals other than the alkali metal chlorides by a Lawrence Smith separation.

Although the chloroplatinate method is held by many to be the most accurate method for the determination of potassium, the cost of the reagent is a serious drawback and necessitates the recovery of the platinum from all residues and its reconversion into hydrochloroplatinic acid.[116,117]

Both the principle and the practice of the perchlorate method run parallel to the separation of potassium and sodium as their chloroplatinates, and as far back as 1831 Sérullas proposed it for the determination of potassium,[118] but it was not until many years later that the method was placed on a sound analytical basis.[119–126,407] It is now widely used, and in many instances, notably in the field of silicate analysis, it has superseded the chloroplatinate method, not only on economic grounds, but also as giving more trustworthy results without any additional manipulation.

The solution, which should contain only the chlorides or nitrates of the alkali metals, magnesium, calcium or barium, is evaporated with an excess of perchloric acid until it fumes strongly, then diluted with water and evaporated to complete dryness. On treating the dry mass with 97% alcohol containing 0·25% of perchloric acid, only potassium perchlorate remains undissolved, together with the perchlorates of rubidium and cæsium, if present. As in the chloroplatinate separation, ammonia fumes must be rigorously excluded throughout the whole determination.

The preparation of lithium and sodium tetraphenyl boron, $XB(C_6H_5)_4$, coupled with the discovery that the corresponding potassium, rubidium, cæsium and ammonium complexes are highly insoluble, has pointed the way to what may well be the most accurate method yet devised for the determination of potassium.[127-131]

Quantitative examination of this new procedure at once indicated its possibilities[127,132,133,407] and subsequently a systematic investigation established that in 0·1N-mineral acid solution the reagent is specific for potassium and ammonium, also for rubidium and cæsium, if present; copper, magnesium, calcium, aluminium, ferric iron, cobalt, nickel, manganese, sulphates and phosphates do not interfere, but mercuric mercury must be absent.[131] After precipitation at room temperature with a solution of pure sodium tetraphenyl boron,[131] the precipitate is filtered off without delay, and washed with a saturated aqueous solution of the reagent before drying to constant weight, but the determination can be completed volumetrically.[134-138] In the presence of ammonium salts the mixed precipitate is filtered off, dissolved in acetone and the ammonium complex alone decomposed by evaporation with a solution of sodium hydroxide until all the acetone has been driven off.[131] When only small quantities of ammonium salts are present the addition of formaldehyde has been recommended.[139]

This new method has already been successfully used for the determination of potassium in biological materials,[134,140] fertilizers,[141] coal ash[142] pharmaceutical preparations,[143] and silicates.[143a]

Among miscellaneous methods for the determination of potassium, precipitation as the perrhenate[144] or periodate[145] is analogous to the perchlorate separation and in both cases the conversion factor is more favourable.

A number of chemists have advocated the use of dipicrylamine and its salts,[146-152] though some unfavourable comment has been reported.[153,154] Other reagents which have had a limited application are picric acid,[155] 5-nitrobarbituric (dilituric) acid,[156,407] zirconium sulphate,[157] sodium 2-chloro-3-nitrotoluene-5-sulphonate,[158,159] and fluoboric acid.[159a] None of the above reagents effects the separation of potassium from rubidium and caesium.

Volumetric Methods.

Among the various methods used for the volumetric determination of potassium, a number depend on precipitation as the cobaltinitrite and oxidation of the nitrite with a standard solution of potassium permanganate[60,160-168] or ceric sulphate.[169-176] Alternatively, a measured excess of the oxidizing agent is added and the excess determined by appropriate back titration, e.g. with sodium oxalate,[177-191] or iodometrically[192-198] with permanganate, or iodometrically[199,200] or via a ferrous salt[201,202] when ceric sulphate is used. A standard solution of chromic acid has also been recommended as the oxidizing agent.[203,204]

Provided that the precipitated cobaltinitrite has the exact composition, $K_2NaCo(NO_2)_6$, 1 ml. of 0·1N-oxidizing agent represents 0·652 mg. of potassium, but this assumption is open to doubt and in a number of instances the use of an empirical factor has been reported.[205-208]

In other procedures, the cobaltinitrite precipitate is either converted into a mixture of neutral chlorides which are then titrated,[209,210] or decomposed by excess of standard acid, followed by back titration.[59,211,212] Here also the accuracy of the determination is based on the above mentioned assumption.

When the potassium has been separated as chloroplatinate, the precipitate is redissolved and reduced and the chloride then titrated;[213-218] alternatively the chloroplatinate can be converted into the corresponding iodo salt by the addition of potassium iodide and the solution then titrated with sodium thiosulphate.[219-221]

Although a volumetric finish has frequently been applied to the old process of determining potassium by precipitation as its acid tartrate,[222-226] it is very doubtful whether the results are of any value except as an approximate method for works control.[227-229] Other volumetric procedures which have been worked out depend on the initial precipitation of the potassium as perchlorate,[230] periodate,[231] potassium calcium ferrocyanide, $K_2CaFeC_6N_6$,[232-234] phosphomolybdate,[235] or phosphotungstate,[236,237] or with dipicrylamine,[238-240] or dilituric acid.[240a] The volumetric determination of potassium after precipitation with sodium tetraphenylboron has already been mentioned (see page 2027).

DETERMINATION BY PHYSICAL METHODS

Physical methods are included among the methods which have been reviewed (see page 2025).

Colorimetry.

A number of colorimetric methods applied to the cobaltinitrite procedure hinge upon the quantitative formation of a compound suitable for colorimetric comparison from either the nitrite or the cobalt content of the precipitated cobaltinitrite. When the approach is through the nitrite, the usual procedure is to form an azo dye from the nitrous acid liberated in acid solution.[241-248] Cobalt gives a stable red complex when treated with Nitroso R salt (disodium 1-nitroso-2-hydroxy-naphthalene-3:6-disulphonate),[249-252,406] and with soluble thiocyanates it forms a deep blue alkali metal cobalt tetrathiocyanate,[253-261] soluble in various organic liquids, and both these compounds have been made the basis of colorimetric determinations.

Among other organic reagents which have been similarly used are indole,[262,263] dimethylglyoxime and sodium sulphide or benzidine,[264-266] choline hydrochloride and sodium ferrocyanide,[267-269] cysteine hydrochloride and hydrogen peroxide,[270] phenoldisulphonic acid,[271] antipyrine,[272] 8-hydroxyquinoline[272a] and ethylenediaminetetra-acetic acid (disodium salt).[272b] A few methods rely on the development of a colour when potassium cobaltinitrite is treated with inorganic reagents.[273-276]

When only small quantities of potassium are to be determined by the chloroplatinate procedure, the colour of the aqueous solution of the chloroplatinate is not sufficiently intense for measurement and either the acid solution is reduced with stannous chloride giving a yellow solution of colloidal platinum,[277-279] or, more usually, chloroplatinate is converted into iodoplatinate and the comparison made through the latter salt.[280-289] Nevertheless, for larger quantities of potassium the use of the aqueous solution of the chloroplatinate is reported to be more advantageous.[290]

The potassium salt of dipicrylamine has been found suitable for colorimetric work[291-301] and, as the technique presents no difficulties, the accuracy of the method depends on the quantitative precipitation of potassium by this reagent. The use of picric acid instead of dipicrylamine has also been proposed,[302,303] but the above limitation also applies to this procedure. Colorimetric methods for the determination of potassium have been reviewed by West.[304]

Polarography.

For the reason already explained (see page 1384), a direct polarographic determination of potassium is not possible, except in a solution containing lithium alone of the alkali metals, without at some stage interposing a chemical separation of sodium and potassium, assuming that the possible presence of rubidium and cæsium can be ignored.

Sometimes, however, only the sum of the sodium and potassium may be needed, and this can be determined with a reasonable degree of accuracy for smaller contents of the two elements, provided that the ratio of potassium to sodium is approximately constant in the different samples under examination.[305-308]

An indirect method for potassium in blood is based on determining the polarograms of a solution of dipicrylamine saturated with potassium before and after addition to the ashed blood serum.[309] In a parallel procedure sodium cobaltinitrite is used instead of dipicrylamine[309a] and in another method the potassium is precipitated with sodium tetraphenylboron, the excess of reagent being determined by polarographic titration.[309b] Like sodium, potassium can be determined polarographically in the presence of up to a 50-fold excess of lithium (see page 1384).

Flame Photometry.

The determination of potassium and sodium by flame photometry is becoming of increasing importance in a number of different analytical fields, not only on account of rapidity in operation but also because of the close agreement of the results with those obtained by the time-consuming classical methods.[310-330]

A review of the literature suggests that the reported interference of other metals may depend to no small extent on the type of photometer used, and on the technique used in preparing the solution;[331-339] otherwise it is difficult to account for conclusions that are at times entirely contradictory. For instance, it has recently been claimed that the accuracy of the determination of the alkali metals in refractory materials is impaired by the presence of aluminium, iron, calcium and magnesium and that appropriate corrections must be made,[340] whereas there is a very substantial volume of evidence drawn from the analysis of clays and ceramic products which entirely negatives this view.[341-349]

When calcium is present in small proportions a photometer with a coal gas burner is advantageous as the temperature of the flame is not sufficiently high to excite many calcium lines and any interference can be eliminated or reduced to negligible proportions by using a suitable filter.[350] Even with high percentages of lime an accurate determination is still possible by employing a reference solution containing lime and sodium and/or potassium in the proportions indicated by an exploratory photometric analysis. For example, the following are certified values for the alkali metal oxides compared with those obtained by flame photometry in a U.S. Bureau of Standards argillaceous limestone containing about 38% of lime:-[351]

	K_2O	Na_2O
Classical	1·17; 1·12	0·34; 0·33%
Flame Photometry	1·16; 1·15	0·36; 0·30%

The presence of barium or zinc[347,352] has been reported to cause interference so appreciable as to necessitate the prior removal of either element.

A study of the effect of common anions on the determination of amounts of sodium and potassium of the order of 10 p.p.m. has shown that nitric acid has no effect up to 1·0 N., at which concentration the interference of sulphuric acid just begins to be apparent, while hydrochloric and phosphoric acids, notably the latter, produce serious interference within the range 0·1 to 1·0 N.[353,354]

Spectrography.

Comment on the spectrographic determination of sodium (see page 1385) applies equally well to potassium, though here there may be a slight bias in favour of an arc technique in which the use of sodium or copper as an internal standard has been recommended.[355-359]

As with sodium, spectrographic analysis is extensively used for the determination of potassium in biological work;[360-371] nevertheless it is often applied to other types of materials,[372-380] especially those in which the concentration of potassium is so low that an error of 10 to 15% in the actual amount of the element is of little or no analytical significance. In favourable circumstances the upper limit at which a satisfactory degree of accuracy is obtainable may be extended to at least 4% of potassium.

Radioactivity.

The β-ray activity of potassium, due to the presence in it of the isotope ^{40}K, has been used for its determination[381-386] and, although a high order of accuracy is not always obtainable, the method has been found useful for control purposes, provided that no other radioactive element is present. Numerous patents have been taken out for an apparatus whereby potassium is estimated by measurement of its γ-radiation,[387-391] and the intensity of the X-ray emission lines from potassium has also been used for the determination of the element.[392,393]

Miscellaneous Methods.

For low concentrations of potassium, turbidimetric measurement of the precipitated cobaltinitrite has been recommended,[394-400] and gasometric methods have been applied by utilizing the reaction between the nitrous acid liberated from the cobaltinitrite and either ferrous sulphate[401,402] or sulphamic acid,[403,404] according to the equation: $NH_2.HSO_3 + HNO_2 = N_2 + H_2SO_4 + H_2O$.

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SECTION LXI

THE BIOLOGICAL PROPERTIES OF POTASSIUM

By F. CALL

INTRODUCTION

Potassium appears to be essential for the maintenance of all forms of life and the internal concentration is closely regulated in the more highly developed organisms by control of the rates of uptake and excretion. Malfunctioning and even death result from a deficiency or an excess of potassium in the organism, and for health the available supply of the element must be maintained within certain limits.

Potassium is found almost universally as the principal inorganic cation inside living cells whereas sodium is the most abundant cation in the extracellular fluids of animals. This distribution of the two cations is maintained by differential permeability of the cell wall combined with active transport of the sodium ion out of the cell. The resultant distribution is partly responsible for the production of bio-electric potentials and is intimately connected with the conduction of nerve impulses and the contraction of muscle. The appropriate section of the Chapter dealing with the biological properties of sodium should be consulted in connection with these topics.

In the present review selection has had to be made from many thousands of references and most articles of purely medical interest have been excluded. Attempts have been made to restrict discussion to the biological properties of the potassium ion, but it has not always been possible to discriminate clearly between the effects of the cation and those of the anion. Most of the common salts of potassium such as the chloride, hydroxide, nitrate, sulphate, etc., have been included when it was clear that the anion, pH etc., did not play the dominant role.

In view of the very wide field the subject has been subdivided under the following headings:

1 Potassium and micro-organisms
2 Potassium and plant growth
    i Occurrence and distribution in soils
    ii Potassium as fertiliser
    iii Occurrence in plants
    iv Deficiency in plants
    v Absorption by plants
    vi Physiological effects on plants
    vii Effects on plant metabolism
3 Potassium and marine or freshwater organisms
4 Potassium and invertebrates
    i Insects
    ii Other invertebrates
5 Potassium and vertebrates
    i Occurrence and distribution
    ii Growth requirements

iii Deficiency
iv Toxicity
v Metabolism
vi Sweat and temperature regulation
vii Excretion
viii Physiological effects of potassium
(*a*) on whole organism
(*b*) on muscle
(*c*) on heart and vascular system
(*d*) on brain and nerve cells
(*e*) permeability and active transport
6 Enzymes

1 POTASSIUM AND MICRO-ORGANISMS

Few actual determinations have been reported of the normal potassium content of micro-organisms. The smooth and rough variants of a strain of *Bacillus proteus* contained respectively 1·9–2·0 and 2·9–3·0% on a dry weight basis.[1] The mycelium of *Penicillium chrysogenum* had a potassium content of 1·0%,[2] agreeing with the lower of the above values, whereas the mycelium of the dry rot fungus, *Merulius lacrymans*, was very rich in potassium.[3]

The growth requirements of micro-organisms for potassium have been reviewed[4] and a positive requirement has been demonstrated for a number of species of bacteria, yeasts and fungi.[5-9] In general, stimulation of growth occurs over a range of concentrations, growth being inhibited at very low and at high concentrations. In some cases the concentration range is very narrow[10,11] and is reported as the optimum concentration for greatest growth of bacteria,[12] flagellates[13] and fungi.[14,15] Analysis of the culture filtrate of *Mycobacterium tuberculosis* shows that potassium is taken up by the culture at a definite rate, 10 μg. of potassium being consumed per mg. dry weight of bacteria.[16] The toxicity of potassium salts as measured by the effects on yeast cells decreases in the order bromide, chloride, nitrate and hydrogen sulphate, the latter being of very low toxicity.[17] Potassium may partially[18] or completely[19] replace the sodium required by halophilic bacteria while sodium may be partially substituted for potassium in the nutrition of *Aspergillus niger*[20] except in the case of extreme potassium deficiency.[21] Rubidium is interchangeable with potassium as regards effect on the growth of bacteria.[18,22] Although multiplication of tobacco mosaic virus in tobacco plants appeared to be independent of the potassium concentration in the nutrient solution,[23] potassium has been shown to be necessary for the growth of influenza virus in chick embryos.[24] Most, though not all, strains of the bacteriophage of *Bacillus megatherium* are rapidly inactivated by solutions containing potassium ions.[25] The rate of reproduction of the parasitic nematode *Meloidogyne incognita* in lima bean plants appears to be limited by the amount of potassium available to the plant.[26]

There have been a number of observations of the effects of potassium supply on the morphology of micro-organisms. Thus, a deficiency of potassium induces the growth of filamentous cells in the bacteria *Clostridium perfringens*[27] and *Moraxella lwoffi*[28] and in the fungi *Candida albicans*[29] and *Actinosphaerium eichorni*.[30] Comparable morphological changes have been observed in yeasts.[31] A deficiency of potassium inhibits the sporulation of a number of species of bacteria[32,33] and fungi,[34-36] similar inhibition also occurring at high concentration of potassium.[37]

The stimulating effect of potassium on the growth of *Micrococcus pyogenes* does not appear to be connected with the metabolism of sugars.[38] Although some evidence has been produced to support the view that potassium is not essential for fermentation, growth or resting metabolism of yeast cells,[39] it is generally agreed that fermentation is stimulated by the element and ceases in its absence.[40,41] There is an antagonistic and competitive relation between the effects of potassium and hydrogen ions.[42,43] Potassium also causes a competitive reversal of the inhibition by sodium, ammonium or cæsium ions of glycolysis bv resting cells of *Lactobacillus arabinosus*.[44] During the initial stages of fermentation by *Escherichia coli* potassium is taken up from the medium by the cells, to be released later. Glucose is used up at an abnormally high rate during this period of potassium uptake.[45] The uptake of potassium is in accordance with a Langmuir type of adsorption isotherm and it is suggested that adsorption sites are created by metabolic intermediates of glucose.[46] Potassium ions appear to be necessary for the formation of fructose 6-phosphate by yeast[47] and for the anaerobic decomposition of pyruvic acid to acetoin by *Lactobacillus arabinosus*,[48] and appear to favour the formation of 3-phosphoroglyceric acid from pentoses by *Escherichia coli*.[49] The rate of acid production by a number of different species of bacteria,[50,51] fungi[52,53] and yeast[54] also increases, often markedly, with the potassium content of the medium. Potassium was found to stimulate, sodium to retard, the respiration of *Azotobacter chroococcum*, the effect being general and not on one particular enzyme system.[55] Potassium also appears to play a part in the formation of acetone by *Clostridium acetobutylicum*,[56] of polysaccharide by *Aerobacter aerogenes*,[57] of fat by *Aspergillus* and *Penicillium* species,[58] in the deamination of aspartic acid by *Proteus X-19*[59] and in the assimilation of amino acids by various species of bacteria and yeasts.[60] The potassium content of the medium has been found to have considerable influence on more complicated processes such as the formation of flavin pigments by *Aspergillus flavus*,[61] of candicidin by *Streptomyces griseus*,[62] and of unknown pigments by *Sterigmatocystis nigra*,[63] on the intensity of luminescence of *Bacterium phosphoreum*,[64] and the optimum temperature for growth of yeast cells[65] and on the antibacterial action of triethanolamine.[66]

Actively respiring yeast cells are found to take up potassium ions from the medium and to release hydrogen ions to the medium, the movements of the ions being reversed when the intensity of respiration slackens.[67,68] Similar ion shifts have been observeu with *Chlorella*[69] and *Bacterium lactis aerogenes*.[70] Although it was at first thought that the uptake of potassium is simultaneous with the formation of glycogen,[71] it is now known that glycogen formation lags behind the ion exchange, which is very rapid, and results from the formation of acid inside the cell, largely succinic acid.[72-74] The enzyme inhibitors fluoride ion and iodoacetate ion cause a loss of potassium from the cell.[75] A similar metabolically regulated ion exchange occurs between sodium and potassium, the electrical potential between cell and medium depending on the ratio of the two ions inside the cell. An oxidation–reduction transport theory has been suggested to explain these phenomena.[76,77]

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2 POTASSIUM AND PLANT GROWTH

The importance of potassium for plant nutrition has been recognised for many years and there are a number of general reviews covering both [illegible] and more recent work.[1-13]

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(i) Occurrence and distribution in soils

The natural potassium content of soils arises from the weathering of rocks and minerals and this process may be still an important source in some soils.[1,2] Some types of lake bottom soils are almost completely deficient in potassium.[3] Analysis of data from the examination of many samples of Mecklenburg soils showed that the soil potassium content is related to soil type, pH or climate. Thus, sandy soils tend to be deficient in potassium, while high rainfall leads to greater leaching of bases from the soil with resulting lowering of pH.[4] In general the vertical distribution of available potassium in a wide variety of soils shows the same pattern, a steady decrease with depth,[5-9] although the actual pattern of variation may depend on the soil type.[9,10] Application of potash fertilisers increases the potassium content of light soils to a much greater depth than for medium or heavy soils.[11,12] Prolonged cultivation may affect the potassium distribution,[13] while a forest fallow results in a decrease of potassium.[14]

Fixation in Soils.

The fixation of potassium by soils with special reference to India has been reviewed.[15] The application of potash fertilisers to soils may result in some or all of the applied potassium being fixed in the upper layers of the soil.[16-22] This fixed potassium may or may not be available to plants and it was early recognised that the clay minerals are responsible for the phenomena. It has been suggested that potassium may exist in soil in four different forms: soluble, exchangeable, fixed (not directly exchangeable) and lattice, the first three forms being in equilibrium with each other.[23] Strong fixation of potassium is found in soils containing montmorillonite. Kaolinitic [illegible] fix insignificant amounts of potassium, but contain large quantities in the exchangeable form. Potassium fixed by montmorillonite soils is released on [illegible] of the soil by calcium ions. More potassium is fixed and made resistant to leaching on drying the soil, indicating that the metal enters into [illegible] lattice of montmorillonite.[24,25] It is possible that in heavily ferti[illegible] alkaline soils montmorillonite may be converted to illite, and such a conversion has been demonstrated experimentally.[26] Illite has been shown to [illegible] in the clay fraction of soils which fix potassium strongly[27] and the formation of this or similar minerals may provide a mechanism for holding potassium in the soil against loss by leaching and yet release the element gradually to plants.[28] Other clay minerals thought to be associated with potassium fixation include the new mineral ammerzodite,[29] muscovite,[30,31] sericite[31] [illegible] microcline fraction of silt.[32,33] The type of clay mineral may deter[illegible] rate of release of the fixed potassium to a form available to plants[34] [illegible] the degree of fixation and the rate of release appear to depend on [illegible] potassium content of the soil.[35] Some soils such as dark chestnut soils may fix potassium without transforming it into the non-exchangeable form.[illegible]

[illegible] experimental studies of potassium fixation the amount available and the rate [illegible] release may be determined after applying electrodialysis,[38,39] leaching with [illegible] solutions[40] or growing crops.[41] All these methods appear to class soils [illegible] the same order as regards availability of potassium. Alternate wetting and drying of soils treated with potassium salt solutions cause rapid fixation of potassium, whereas little fixation occurs when the soil is kept continuously moist.[42,43] Fixation is greater from solutions of potassium carbonate than from solutions of the chloride.[44,45] The effects of other additional ions differ with the ion species, with the concentration and perhaps with soil type. Thus, sodium chloride may diminish fixation,[44] increase it[45] or have no effect.[46] Calcium salts appear to increase fixation[47-49] but this may be due to changes of pH.[50] Soils containing fixed potassium ion have little or no fixing power for ammonium ion.[51,52] It is interesting to note that fixed potassium promotes the fixation of atmospheric nitrogen by *Azotobacter*; the effect of potassium ion in free solution on this nitrogen fixation is much less.[53]

Exchangeable Potassium in Soils.

A definite relationship has been demonstrated between the soil content of exchangeable potassium and the yield of crops grown in that soil.[54-56] Humus and leaf litter do not appear to bind potassium as an exchangeable cation although calcium may be so bound.[57] In soils potassium is steadily converted from an unexchangeable to an exchangeable form in the presence of a growing crop[58] and nitrifying bacteria have been shown to cause the conversion of the potassium of leucite to an exchangeable form in the presence of exchange resins saturated with ammonium and phosphate ions.[59] The order of the increasing stability of the minerals occurring in soil (increasing resistance to exchange of potassium) is: kaolin, muscovite, microcline and montmorillonite, [illegible] that exchangeable potassium should be largely associated with mica and kaolin.[61,62] The particle size of these minerals has, however, been shown to affect the adsorption strongly.[63] It has been claimed that most of the exchangeable potassium in soil exists as hydrated potassium aluminium silicate (potassium zeolite)[64] and the hydrolysis of such artificially prepared zeolites has been studied. The calculated values of the concentrations of potassium ions in the soil solution agree very closely with typical experimental values.[65] The amount of potassium released by soils on leaching with solutions of different acetates depends on the predominant cation in the leaching solution and it is found that ammonium acetate gives the best estimate of exchangeable potassium.[66] The total exchange and also the relative amounts of cations exchanged in soils vary with the moisture content of the soil and with the soil type.[67] The concentration of potassium ions in the soil solution depends also on the ratio of the concentrations of calcium to potassium ions in the soil.[68-74] The activity of potassium in a number of clays and clay minerals is increased by calcium[75-77] and by magnesium.[78] The energies of exchange of calcium by potassium in soils have been computed from the cationic composition of water extracts of the soils and it is found that energies ranging from −3500 to −4000 g.-cal. are associated with potassium deficiencies in plants, while energies from −2500 to −3000 g.-cal. are satisfactory.[79] Phosphate fertilisers also increase the solubility of soil potassium[80,81] while potassium salts decrease the retention of phosphate ion.[82] Both ammonium chloride and ammonium sulphate increase the exchangeable potassium content of soil, the former salt having the greater effect.[83,84]

Movement and Leaching in Soils.

In many soils a large proportion of potassium salts applied to the soil is rapidly removed by leaching. The rate of leaching is influenced by cultivation,[85,86] the pH, the rate of percolation and the level of exchangeable potassium in the soil.[87] Leaching is less under crops, since transpiration and surface evaporation reduce the proportion of surface water infiltrating.[88] In some soils exchangeable potassium lost by leaching may be replaced by release from fixed potassium.[89] Loss of potassium by leaching is greater in sandy than in clay soils.[90] The rate of loss is at first great but falls off with continued irrigation.[91,92] Potassium tends to accumulate above the packed layer of soil resulting from ploughing (plough-sole) except when the soil contains much humus which forms soluble salts with potassium.[93] Studies of the movement of potassium in different soils show that in general the element tends to accumulate in the B_1 horizon.[94,95] Other ions have an effect on the rate of leaching. Thus ammonium sulphate increases the rate of movement, while phosphate appears to fix the potassium and reduce the rate of movement.[96-99] Calcium ions also reduce the loss of potassium by leaching.[100] Accumulation of potassium in the B horizon is much greater when a potash fertiliser is applied once in four years than when the same amount is applied in four equal annual additions.[101] Erosion by surface run-off from a black soil was found to remove largely the silt fraction which, however, contained four times as much potassium as the remaining whole soil.[102] The rate of loss of potassium by leaching of synthetic zeolites has been found to follow a simple logarithmic equation.[103]

Availability of Soil Potassium to Plants.

Soils treated annually with potash fertilisers over a period of years may contain no more water-soluble potassium than untreated soils,[104] owing to conversion of the potassium to non-exchangeable forms. In many cases plants are able to draw on non-exchangeable potassium when this has sufficient solubility.[105-109] Minerals may be ranked in the following order of decreasing ease of release of potassium ions to plants: muscovite, greensand, microcline.[110]

Bentonite does not readily release potassium ions to tomato plants.[111] Release of potassium from non-exchangeable forms is highest in the finest fractions, *i.e.* in the clay fraction.[112] The ploughing of crops into the soil does not appear to increase the available potassium content in proportion to the potassium returned to the soil.[113] Pot experiments with a single soil have shown that the deeper subsoil is richer in readily available potassium than are the shallower sub-soils.[114] There is general agreement that assimilable potassium increases with pH, acid soils tending to be deficient,[115-119] although uptake by plants is higher in acid soils. The level of available potassium in soil has been observed to increase during the period of growth of a crop,[120] an effect which may be due to increased biological activity in the soil.[121] Certainly available potassium is higher in the rhizosphere of a wide variety of crops[122] and also increases with the humus content of the soil.[123,124] The availability of potassium may be affected by the water supply, the effect depending on the plant and the soil.[125,126] Liming reduces assimilation of potassium[127-129] and there is some evidence that this effect is due to a reduction of availability.[130,131] Available potassium is not affected by additions of sodium chloride[132] but is increased by fertilisation by superphosphate.[133]

Determination of Available Potassium in Soil.

Considerable effort has been devoted to determining the amount of potassium in soil that is available to growing plants. The methods developed may be sharply divided into chemical methods which ultimately rely on chemical analysis and biological methods which depend on the response of some organism. Although simple chemical analysis of the soil is insufficient to determine the assimilable potassium,[134] satisfactory rapid chemical tests have been based on determination of the amount of potassium extractable from the soil.[135] The potassium content of soil extracts may be determined by a volumetric[136] or turbidimetric[137] modification of the cobaltinitrite method, or the flame photometer may be successfully employed.[138] The soil extract may be obtained by electrodialysis,[139] by leaching with solutions of ammonium nitrate[140] or by extraction with hydrochloric acid,[141-146] nitric acid,[147] acetic acid,[148] citric acid[148] or ammonium acetate.[141,147] In each case the conditions of extraction must be carefully standardised.

Of the biological methods for estimating available potassium, one of the most widely used is the Neubauer seedling method.[149-153] In this method seeds, usually of rye, are germinated in the presence of a known amount of the soil under test and after a fixed period, usually twelve or fourteen days, the seedlings are removed, ashed and the potassium content determined chemically. Among the many factors affecting the absorption of potassium in this test that have been studied are the presence of other ions, particularly calcium,[154-156] the pH of the soil,[157] the species of seeds,[158] and the effect of light.[159] A variant of the Neubauer method is to culture the fungus *Aspergillus niger* in a medium to which soil or soil extract has been added and to assess the available potassium by the increase in weight of the mycelium in a given time under controlled conditions.[160-164,197] The effect of other salts on growth of the fungus has been studied.[165] The Mitscherlich pot culture method is based on the yields of plants grown in sand to which the soil under test has been added.[166-168] Chemical analysis of the potassium content of leaves, petioles and plant juices has also been used to assess the potassium requirements of soils.[169-172] Proper sampling of soil in the field is very important since the available potassium may vary at different depths as well as in different areas.[173]

Comparative studies indicate that the degree of correlation between any soil test and crop yield is far from perfect[174] and the ratio of potassium to other cations may be a more reliable index of soil productivity than is the total exchangeable potassium.[175] The various extraction procedures do not always give comparable results, depending on the soil type and cultivation practice.[176-180] There is some measure of agreement that the closest estimate of assimilable potassium is obtained by extraction with nitric acid, with citric acid extraction as next best.[181-186] The percentage accuracy of prediction of potassium deficiency given by chemical methods is found to depend on the actual crop being grown, being highest with cotton and lowest with certain legumes.[187] Electrodialysis as an extraction procedure tends to remove rather more potassium than is available to plants.[188-190] The Neubauer test in general gives a satisfactory estimate of available potassium[191-194] but tends to overestimate this in calcareous soils.[195,196] The *Aspergillus* method usually agrees with the Neubauer method but may fail on certain soils.[197,198] The use of pot experiments to determine available potassium may give results disagreeing with large scale crop production[199] and may be of doubtful value for assessing the need for fertiliser.[200,201] Crop analysis would appear to be better for assessing the fertility level of a soil with respect to potassium.[202,203]

Effect of Cultivation on Soil Potassium.

Straw mulching causes a definite increase of exchangeable potassium in orchard soils to a depth of twenty four inches.[204-206] Farmyard manure and dunging also increase the exchangeable potassium in soils and this is reflected in higher potassium contents in crops grown with such treatments.[207-210] Repeated use of potash fertilisers did not cause an increase in the level of exchangeable potassium in soils.[211,212] Exchangeable potassium is greater in soils treated with potassium dihydrogen phosphate than in those treated with potassium chloride plus calcium phosphate.[213] Potassium chloride improved the structure of some soils of low permeability,[214] but had no effect on other soils.[215] This fertiliser also tended to increase the pH of some soils but not sandy soils and those containing much calcium.[216-218] Repeated heavy dressings of potash fertilisers caused a large increase in the soil population of protozoa and of *Azotobacter chroococcum*.[219] A temporary increase in soluble potassium occurs in soils treated with steam or with most common soil fumigants with the exception of propylene oxide or ethylene dibromide.[220-222]

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(ii) Potassium as fertiliser

Nutrient Solutions.

The complex effects of potassium on plant growth may best be investigated by watering plants growing on sand with solutions containing potassium and

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other salts. Such techniques have shown that the minimum concentration of potassium in the solution to maintain optimum growth depends on the species of plant, ranging from 0·5 p.p.m. for cow peas, oats and soy beans[1,2] to 40 p.p.m. for tomatoes.[3] Even more important, however, are the relative proportions of nutrient salts in the solution, not only the well-known nitrogen–phosphorus–potassium ratio[4-7] but including also the ratio of potassium to calcium and magnesium.[8-10] The potassium–iron ratio is found to have some influence on the magnitude of pH changes in nutrient solutions.[11] The anions associated with potassium appear to have very little effect on growth.[12] Foliar fertilisation, which depends on the absorption of potassium salts, usually the phosphate, through the leaf, is carried out by spraying the leaves with a solution of the salt when the humidity is high. Treatment with potassium dihydrogen phosphate is effective when the soil is lacking in phosphates.[13] A considerable increase in the bitter principle of hops occurred when cuttings were treated with solutions of potassium bromide or potassium alum, the latter salt being more effective.[14] Hardening of tomato plants in nutrient solutions rich in potassium gave reduced yields over plants set out tender.[15]

Crop Response.

Crops respond chiefly to fertilisation with potassium salts by giving increased yields,[16-21] but additional advantages have been recorded. Thus, potash fertilisers have been stated to depress the growth of weeds and moss,[22] to reduce cotton wilt infection,[23] to increase the quantity and strength of cereal straw[24-26] and to increase the sugar content of grapes[27] and of sugar cane.[28] The response to fertilisation may be several years in reaching its maximum and may be maintained for some years after fertilisation is stopped.[29] The response of crops to fertilisation also depends on the level of the exchangeable potassium in the soil, for if this is below a certain minimum value a profitable yield response is obtained, the minimum level depending on the crop and the soil.[30-32] The Mitscherlich curves connecting both total and partial plant yields with potash fertiliser applications are curved, the departure from linearity being ascribed to variation in the potassium contents of different parts of the plants.[33] A reduction in the potassium supply to bean plants reduces nitrogen fixation by the root nodule bacteria.[34] In clover different cultures of the nitrogen fixing bacteria *Rhizobium trifolii* were found to respond in very different degrees to fertilisation by potassium.[35] Potash fertilisers have been shown to cause a large increase in soil bacterial activity, nitrification but not ammonification being increased.[36]

Effect of Other Nutrients on Potassium Fertilisers.

The effect on plant growth of potassium salts depends largely on the relative proportions of mineral nutrients in the soil, in particular on the nitrogen–phosphorus–potassium ratio. The optimum ratio of these three essential nutrients for maximum growth depends on the crop, the soil type, climate, etc., and often an excess of one element will cause a drastic reduction of yield. The actual ratio of the contents of these three elements in plants may be quite different from the optimum ratio required in fertilisers.[37-40] Careful analysis of the results of fertiliser trials indicates that certain specific effects can be ascribed to potassium. Thus, increasing the proportion of potassium in a mixed fertiliser tends to increase the resistance to lodging of grain by increasing the amount of sugar transformed to structural materials in the stem.[41] Potassium also has a favourable effect on the development of gladioli bulbs,[42] increases the oil content in tung trees[43] and causes cotton to fruit earlier.[44] The ascorbic acid of spinach is more stable after heavy applications of potassium fertilisers.[45]

The actual amount of potassium taken up by plants depends on the relative proportions of nitrogen and phosphorus available to the plant[45-48] as if the plant could utilise the three essential elements only in certain definite proportions.[49] It has been observed that when only two of the three critical elements, nitrogen, phosphorus and potassium, are applied to a soil the absorption of the third element is depressed on an infertile soil but is increased on a more fertile soil.[50] The actual plant uptake also depends on the species of plant. Thus an increase in the ratio of nitrogen and phosphorus to potassium results in an increased ratio of nitrogen to potassium in flax leaves but no change in wheat which is able to adjust itself to the changed fertiliser ratio.[51] Alfalfa strongly absorbs potassium and may exhaust the soil to the detriment of succeeding crops.[52]

The uptake of potassium by plants depends on the level of phosphate available in the soil.[53,54] Similarly application of unusually high levels of potash fertilisers tends to depress the uptake of phosphate,[55,56] although in some circumstances potassium sulphate may increase the absorption of phosphate by its effect on the soil pH.[57] The ratio of calcium and of magnesium to potassium also has important effects on crop yields.[58-60] An increase in the proportion of calcium tends to reduce the assimilation of potassium but magnesium has little effect.[61,62] Magnesium salts applied alone lower the starch content of potatoes, whereas when applied in conjunction with potassium they increase the starch content.[63] The ratio of calcium to potassium in the soil has an important influence on the burning properties of tobacco.[64]

Effect of Anion of Potash Fertilisers.

Many crops show no difference in response to fertilisation with potassium chloride or potassium sulphate except that at high levels of application the chloride ion may have harmful effects on some plants.[65-68] Potassium chloride may cause an increase in the concentration of calcium chloride in the soil which may harm sensitive plants.[69,70]

Potassium nitrate appears to be a less effective fertiliser than the sulphate and under certain conditions has caused injurious effects on plants.[71-73] Kainite has been found to give better yields in general than other potassium fertilisers with a wide range of crops.[74-77] Comparative tests with a number of mixed potassium salts indicated that the effectiveness varied inversely with the percentage of potassium in the salt.[78] A greater percentage of potassium was fixed by acid soils from potassium carbonate than from the sulphate or chloride.[79] The actual potassium salt to be used in any particular instance may depend on the form in which the nitrogen and phosphate fertilisers are applied and also on the soil type.[80] Insoluble potassium salts do not seem to be effective as fertilisers, for very little potassium is absorbed from finely ground orthoclase,[81] granite,[82] feldspar[82] or sericite[83] applied to crops.

Replacement of Potassium by Sodium in Crop Fertilisation.

The replacement of potassium as a plant food by sodium has been discussed in detail elsewhere (Volume II, Supplement II, pages 1404 and 1405) and the following additional observations apply particularly to the role of sodium in fertilisation. Many crops respond favourably to a mixture of sodium and potassium salts[84,85] and maximum yields may be obtained with as much as half the potassium replaced by sodium. In some cases sodium appears to increase the absorption of potassium by the crop but in others sodium itself is absorbed and replaces potassium inside the plant.[86-88] Gradual replacement of potassium by rubidium in fertiliser salts decreases the yield of oats and is harmful to grain formation.[89]

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(iii) Occurrence in plants

The actual level of potassium in plants depends on numerous factors and a study has been made of the effect on the potassium content of the leaves of pears of variety, soil management, date of sampling and season.[1] The potassium content of many winter crops is high and varies little at high moisture contents but is very variable when the crop is dry.[2] Determinations have been made of the potassium contents of many weeds and wild plants under various conditions of growth and at different seasons.[3-8] There have been a number of determinations of the potassium content of many Chinese crops and food plants.[9-11] Tobacco averages 2·40–2·50% on dry weight for both American and New Zealand samples;[12,13] grasses average about 3·00%;[14-17] wheat varies from 1·13 to 3·32% depending on variety;[18] the pinnae of different varieties of date palm similarly vary from 0·232 to 0·776%;[19] the seeds of conifers vary from 0·5% (spruce) to 1·3% (larch).[20] There is a wide range in the potassium content of grapes[21,22] and wines.[23]

There are many difficulties in the localisation of potassium inside cells and tissues by histochemical methods[24,25] but there is no evidence of the definite localisation of the element in the cytoplasm or the nucleus, the salt being found chiefly in the vacuoles. Apical buds and the tips of stems and roots appear to be poor in potassium when dormant but become rich when active.[26,27] A considerable range of variation occurs in the potassium contents of different parts of the leaves of tobacco[28] and tung[29] and also between the leaf, sheath and stem of the grass, *Panicum antidotale* Retz.[30] Potassium tends to accumulate in the tuber of the potato,[31] in the fleshy roots of the sweet potato[32] and in roots of sugar beet.[33] The concentration of potassium appears to be lower in the fruit than the leaf of tomato[34] but, owing to its greater weight, the fruit contains the major part of the potassium of the plant.[35] The mean content of pineapple fruit is also lower than that of other parts of the plant.[36] In winter 62% of the potassium of the grape vine is found in the leaves and twigs and the large increase in potassium in the maturing grapes does not appear to come from the stem.[37] The potassium content of the rind of the sugar beet is higher than that of the pulp.[38] The changes in the potassium contents of the wall and pulp of cacao fruits during development[39] and of the various parts of the seeds of citrus fruits have also been studied.[40] Analyses have also been made of the ash composition including the potassium content of leaves, bark, wood and roots of aspen, *Carex pilosa*, tree fern, oak and hazel,[41] and of the leaf, footstock and root of *Eutrema wasabi*.[42]

Foliar Analysis.

A great deal of attention has been devoted to developing the method of foliar analysis for the diagnosis of the potassium status of soils. In this method selected leaves are ashed and their potassium content is determined and interpreted as a measure of the available potassium in the soil. The many difficulties and pitfalls of such a method may be inferred from the following observations. The potassium contents of leaves taken from the same tree at the same time may differ widely (e.g. from 0·63 to 1·68% on dry weight in the case of orange) and a sufficient number of leaves must be taken to ensure that the required precision is attained.[43] Similar variations have been found in grain.[44] The potassium concentration decreases with the age of the leaf,[45] so that the upper leaves of a shoot tend to have a higher potassium content than the lower,[46-48] though this trend appears to be reversed in tung trees.[49] The upper section of wheat straw is richer in potassium.[50] The mean potassium content of leaves of trees growing on the same soil and sampled at the same time depends markedly on the variety and root-stock of apples,[51-53] citrus[54,55] and tung.[56] Leaves from bearing apple trees were lower in potassium than those from non-bearing trees.[57] The leaves of sterile oil palms were similarly richer in potassium than the leaves of producing trees.[58]

The general technique of sampling and analysis has been discussed.[59,60] In addition several specialised techniques have been evolved, for example a method of ashing and treating leaves which is claimed to show the distribution of potassium in the leaf and so enables potassium-deficient leaves to be separated from healthy leaves.[61] Methods have also been developed for the extraction of sap from leaves and stems.[62,63] Experience with apple trees suggests that it is desirable to sample leaves from a definite part of the leader shoot, avoiding the top leaves.[64,65] It is also satisfactory to analyse samples of bark obtained during the period of dormancy.[66] The application of foliar analysis has been recommended for the grape vine,[67-69] rubber plant,[70] barley,[71] pine[72] and birch[73] but was found to be less useful for tobacco[74] or fruit trees including peach, prune and almond,[75] where critical values of the potassium content could not be established. In one variety of apple no definite relation was found between potassium content in the foliage and quality of fruit.[76]

If the potassium content of the leaves obtained by foliar analysis falls below the critical values given in Table I the plant is on the verge of suffering from potassium deficiency and potash fertilisers should be applied at once.

TABLE I.- CRITICAL POTASSIUM CONTENTS OF LEAVES

Species	Potassium per cent.	Ref.
Apple	0·75	77
Apple	0·65	78
Apple	1·25	79
Apple	1·18	80
Boysenberry	0·50	94
Carrot	0·32	81
Cherry	0·75	82
Citrus	0·20	83
Citrus	0·20	84
Clover	0·8	85,87
Clover	1·0	86
Grape	0·75	88
Macadamia temifolia	0·6	89
Mathiola incana.	1·5	90
Maize	1·2	92
Peach	1·0	93
Peach	2·46	80
Peas	0·36	81
Raspberry (black)	0·20	94
Raspberry (red)	1·0	95
Raspberry	0·7	96
Sugar cane	0·4	97

There is usually a seasonal variation in the potassium content of any particular plant organ or tissue. Thus the potassium content of the leaves of deciduous trees such as beech, birch and oak rises to a maximum in July or August and then falls steadily until defoliation when about 45% of the potassium may pass back into the trunk.[98-100] In conifers potassium tends to accumulate in the stems in winter and to transfer gradually to the needles in early summer.[100] The potassium content of grasses also shows a cyclical variation between a minimum in winter to a maximum in August,[101] but in the leaves of the date palm the content increases slowly until the leaf is one year old and then decreases slowly.[102] The juice from the stems and leaves of alfalfa varies in potassium content throughout the day.[103] The potassium content of alfalfa[104] and of tobacco[105] is highest at first harvest and decreases with later cuttings. In many species the percentage of potassium decreases with the age of the plant.[105] As the crop ripens potassium moves from adjacent leaves into the seed husk in cotton[107] and into the fruit in olives[108] although the potassium content of the latter falls somewhat as ripening is completed. Potassium reaches a maximum in the wheat plant at four weeks before harvest and then declines to about half this value at harvest.[109-112] A similar trend occurs in maize, the maximum being reached about three weeks after silking and little accumulation taking place in the grain.[113] Studies on the pecan nut indicate that the decline in the apparent potassium content of the kernel may be due to the very rapid rate of increase of the dry weight at maturation.[114] In bracken the potassium content of the rhizome is relatively constant throughout the growing season, while the content of the fronds decreases with age.[115] The potassium content of leaves falls more rapidly than usual in grape vines suffering from potassium deficiency.[116] In lime-induced chlorosis, on the other hand, potassium may show an abnormally large increase in midsummer instead of the normal decrease.[117] The fall in potassium in orange leaves at blossom time and at abscission coincides with the accumulation of carbohydrate in the leaves and may be the result of this.[118] It has been suggested that the return of potassium from the leaves to the trunk is in order to fulfil some unknown function rather than to conserve potassium.[119] Most of the stored potassium moves out of soybean cotyledons at about the same rate as the organic materials such as sugars, only about one third of the potassium remaining at emergence of the cotyledons.[120] When the supply of potassium to the plant is deficient the potassium tends to accumulate in leaves adjacent to the growing point and to move into this as the season progresses.[121] This movement into the youngest leaves appears to be general and to occur in many species.[122,123] Where seeds are produced, the potassium tends to move from the leaves into the seeds,[124] and such movement may cause the potassium content of fruit-bearing orange branches to be only half the content of non-bearing branches.[125] The probable rate of translocation of potassium is too rapid to be attributable to diffusion alone and it has been suggested that movement occurs in the form of salts of amino acids or of proteins.[126] The trunk, stock and root system of apple trees have been found to store sufficient potassium to promote fair growth of the shoots the next season when no potassium was supplied.[127] Nitrogen supplied in the form of nitrates appeared to stimulate the resorption and transport of potassium in flax.[128]

Many attempts have been made to relate the potassium content of plants to the available potassium of the soil and in general there is good correlation for a wide variety of crops.[129-133] The type of soil does play a part in regulating the absorption of potassium; thus absorption is less from clay soils than from sandy soils[134] while absorption is also reduced from calcareous soils.[135] In many instances the potassium content of crops is correlated with the amount of exchangeable potassium in the soil[136,137] the relation between the two forms of potassium being linear in some cases.[138] Other investigators have found better correlation between plant potassium and the percentage saturation of potassium in the soil.[139]

Soil treatments affect the uptake of potassium considerably. Thus, the type of mixed fertiliser applied affects the content of potassium and its ratio to nitrogen and phosphorus in the grape vine.[140] Green manuring increases the content of root-soluble potassium in the soil.[141] Although application of magnesium to soil appears to have little effect on the potassium content of blueberry leaves,[142] the potassium content of corn leaves shows a significant negative correlation with the magnesium content of the leaf.[143] The potassium content of chestnut leaves and twigs tends to vary inversely with the calcium content,[144] whereas alfalfa tends to accumulate more potassium than it needs unless the soil contains a high level of calcium.[145] An increase in the calcium supplied to soya bean plants lowers the potassium contents of the leaves and stems and increases the amount utilised for seed production. Calcium has a greater effect on potassium distribution than has magnesium.[146] The sum of the cations calcium, magnesium and potassium determined in maize leaves at silking time tends to be constant at about 100 milliequivalents per

100 g.[147] The relative amounts of these three cations taken up by plants also depend on the nature of the clay colloids of the soil and on the percentage saturation of the colloid by the cations.[148] Copper tends to reduce the potassium content of many crops.[149,150] The potassium content of crops is also affected by the moisture tension prevailing in the soil[151] and the general irrigation practice.[152,153] Two species of amphibious plant, *Lysimachia* and *Alisma*, had much higher potassium contents when grown in water than when grown in soil.[154] Considerable amounts of potassium nitrate are taken up by the halophyte desert plants, *Anabasis aphylla* and *Halocnemum strobilaceum.*[155] Treatment of the soil with certain soil fumigants may cause an increase in the potassium content of plants.[156] Studies with plants grown in nutrient solutions indicate that the potassium content of leaves depends mainly on the concentration of potassium in the nutrient solution,[157] the leaf content of some species increasing arithmetically as the concentration in solution increases geometrically.[158] Although the relative concentrations of other cations have some effect on the potassium content of leaves,[159,160] the absolute concentration of potassium in solution is the most important single factor governing accumulation in leaves.[161] Maximum growth of many coniferous and deciduous seedlings appears to occur at an optimum internal potassium concentration of 1•50–1•72%.[162]

Three stages have been observed during the growth of rice in nutrient solutions of various concentrations. These are: the deficiency stage when both the yield and the potassium content of the plant increase with increase of potassium concentration in solution over the range 0–4 p.p.m., the normal stage when the yield increases but the potassium content remains constant over the range 4–16 p.p.m., and finally the luxury consumption stage when the potassium content of the plant increases but the yield remains constant at nutrient concentrations greater than 16 p.p.m.[163] Similar stages have been demonstrated with other crops such as potatoes[164] and sugar cane[165,166] and the phenomenon may be widespread. The potassium content of potato leaves shows a good correlation with the yield[167] but this is not true for the tuber potassium content.[168] Increased yields obtained by growing tomatoes in the greenhouse were inversely related to the potassium content of the leaves and it appears that other nutrients are more important in regulating yield than potassium.[169] There is no clear correlation between the potassium content and the yield in sugar beet and a supply of sodium appears to be required by this plant even when adequate potassium is available.[170,171] A minimum content in the petioles of 2•00% is necessary for yields of 3•5 tons per acre of grapes,[172] and similar contents are required for high yields of many farm crops.[173] The maximum drug content of *Digitalis purpurea* occurs at a leaf content of 1•50% K.[174] Heavy fruiting in the avocado lowers the potassium and phosphorus reserves of the trees and it is suggested that this may be one factor in the alternate bearing characteristics of this plant.[175]

It is claimed that potassium occurs in plants not only in an ionic, dialysable form but also in a non-dialysable form. Thus, in peas 48% and in potato stems 30•4% of the potassium is stated to be dialysable, but sugar beet and tomatoes have much higher percentages of ionic potassium.[176] Water and sometimes acids often fail to extract completely the potassium from plant tissues and it is suggested that the unextractable potassium may be bound to proteins.[177,178] Adequate leaching with water, however, indicates that in many species of plants the potassium is completely ionic and water-soluble.[179-183]

Careful determinations of the atomic weight of potassium isolated from the ash of sugar beet and potato plants show that there is no concentration of the isotope of atomic weight 41 during growth[184-186] as has been claimed.[187]

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(iv) Potassium deficiency in plants

A plant may be said to be deficient in potassium when the potassium content of the plant becomes reduced through any cause to such a low level as to affect the health of the plant, as evidenced by typical visible symptoms. There have been several extensive reviews of potassium deficiency symptoms in plants[1-7] and references to reports on individual species are listed in Table II.

In some species potassium deficiency symptoms appear extremely early, before signs of deficiency of, or toxicity due to, any other element.[18] The most typical visual symptoms occur in the leaves and take the form of areas or spots of chlorosis, marginal scorching, browning and rolling or curling of the leaf. Later, leaves undergo necrosis and suffer premature fall.[44,52,55] These leaf symptoms are often so characteristic that they were given specific names and regarded as typical of a disease before the precise cause was known, e.g. alfalfa yellows,[9] curl leaf of cherries,[33] burnt leaf of citrus[36] and potato fire blight.[70] Marked varietal difference has been found in potassium

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TABLE II.- REPORTED VISUAL SYMPTOMS OF POTASSIUM DEFICIENCY IN PLANTS

Plant Species	Reference	Plant Species	Reference
Ailanthus	8	Mustard	28
Alfalfa	9	Napier grass	57
Apple	10-15	Narcissus	58
Azalea	16,17	Oats	19,20,59,60
Barley	18-20	Olive	61
Beans	12,42	Onions	12
Beet	21	Orange	62
Blueberry	22	Passion fruit	36
Bracken	23	Pea	72,73
Brassica napus	24	Peach	63-65
Cabbage	21,25,26	Peanut	66
Cacao	27	Pear	13
Camelina sativa	28	Pecan	67
Carnation	29,30	*Pennisetum purpureum*	57
Carrot	20,21	Pine	68,69
Cassava	31	Poppy	28
Castor oil plant	28	Potato	12,70,71,73
Catalpa	8	Rape	24,28
Cherry	32,33	*Raphanus oleiferus*	28
Chrysanthemum	30	Rice	74
Citrus	34-36	Rutabaga	19
Clover	19,37-39	Salvia	20
Colza	28	Soy	28,42,75
Cotton	40,41	Spinach	20
Cowpea	42	Spruce	47
Daffodil	43	Strawberry	76,77
Fir	47	Sugar beet	20,78,79
Flax	28,44-46	Sugar cane	80-84
Gladiolus	48	Sunflower	85
Grape	49-52	Tea	86-88
Hemp	28,45	Tobacco	12,20,89,90
Hevea brasiliensis	53	Tomato	12,91-95
Jute	28	Tulip	43,58
Kudzu	54	Tung	96
Larch	47	Ulminis	8
Lettuce	55,56	Wheat	20,97
Linseed	46		

deficiency symptoms in strawberries.[77] The chief symptom in tobacco is a very characteristic yellow mottling of the leaves[90] but the burning qualities of tobacco are so markedly affected by the potassium content of the leaf[89] that a deficiency is recognised whenever a loss of quality occurs.[98] Potassium deficiency also reduces the sugar content of sugar beet,[79] delays maturation and reduces the number of fruits per plant in tomatoes,[91] causes strawberries to yield smaller fruits[76] and reduces the secretion of nectar by winter rape.[24] Two types of potassium deficiency symptoms have been observed in tomatoes. In the first stage the plants are stunted, hard and yellow, in the second stage the plants begin to grow, turn green and become soft. The first stage is associated with a high carbohydrate content, the second stage with a greatly diminished content.[9] Leaves showing scorch through lack of potassium show not only a lower potassium content but also a steeper potassium gradient from base to apex than unscorched leaves.[99] Plants such as hemp or flax if deficient in potassium produce a looser and thinner-walled group of bast cells,[45] and such changes in the cell walls may be responsible for the structural failure of vascular tissue observed in deficient tomatoes.[95] Potassium starvation causes a reduction not only in the size and number of seeds[40] but also in their germination number, starch[100] and oil[96] content. The bulb weight increase of tulips and narcissus is also reduced by potassium deficiency.[58] The absence of potassium produces a greater retardation of growth in *Hevea brasiliensis* than does the absence of any other element.[53] A number of observations suggest that plants deficient in potassium are less resistant to disease caused by bacterial or fungal attack.[101] Thus, clubroot in crucifers appears to depend on potassium supply.[102,103] The calyx end of potassium deficient apples remains open thus permitting fungus spores to enter the core.[11] Potassium starvation also appears to favour cotton rust[41] and 'blighty wheat' or blackening of the ears caused by various fungi.[97]

Evidence is accumulating that many deficiency symptoms are caused by an upset of mineral nutrient balance, so that a deviation from the optimum supply of potassium, for instance, may affect the uptake of other essential anions or cations and thus produce changes in the health of the plant. The response of plants to potassium deficiency has been shown to depend on the nitrogen supply[27,104-106] and symptoms often appear with a high nitrogen and a deficient potassium supply and vice versa.[107-110] Potassium deficiency may cause an excessive accumulation of boron in lemon plants and boron toxicity symptoms may appear, while too high a potassium supply may cause boron deficiency.[111,116] Calcium behaves in a very similar way to potassium[112] and there is some indication that the calcium–potassium ratio has an important effect on the boron uptake.[113] Boron reduces the requirement of flax for potassium.[114,115] The absorption of potassium by plants appears to be inversely related to the absorption of calcium and magnesium.[116-119] The incidence of potato leaf scorch is highest on soils with high calcium to potassium ratios.[120] Calcium and potassium are next to nitrogen in importance in affecting growth.[121] The uptake of magnesium has been shown to depend on the magnesium–potassium ratio in the soil and an excessive supply of potassium may cause magnesium deficiency with resulting chlorosis.[122-124] Although it is well known that sodium can replace potassium to some extent in some plants, symptoms of potassium deficiency have been observed in crops grown in salty soils following inundations by the sea.[125] Iron and potassium appear to be interrelated in the metabolism of the potato plant. Thus iron has an inhibiting effect on the appearance of potassium deficiency symptoms, although these delayed symptoms may become ultimately more severe.[126-127] An excessive supply of iron and potassium also produces symptoms in the leaves of potatoes.[128] Potassium-deficient sugar cane absorbs more iron than the normal and this excess becomes localised in the nodes, a fact which was once made a test for potassium deficiency in this species.[129] Extra aluminium is taken up by tomato plants deficient in potassium.[130]

The effects of potassium deficiency in plants have been studied in an attempt to discover the role of potassium in plant metabolism and growth.[131] Potassium deficient *Chlorella* shows an increase in respiration and a reduction of photosynthesis.[132] If Valencia oranges are deprived of potassium for a number of years, the fruit juice is found to have an increased concentration of sugars, and decreased concentrations of ascorbic and citric acids;[133] since potassium is an essential base in the buffer system of many plant juices, the pH of these is lowered.[134] Potassium deficiency interferes with protein synthesis, so that ammonia and amide nitrogen, total and reducing sugars all

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increase at first.[85,135-140] Later the carbohydrates may fall again. Both chlorophyll and carotene are reduced in chlorotic leaves from potassium deficient apple trees,[141] while deficient barley leaves are found to contain putrescine. Application of putrescine to leaves of normal plants incited the characteristic symptoms of potassium deficiency.[142]

Several attempts have been made at first-aid treatments for potassium deficient plants. Leaf scorch on fruit trees has been successfully prevented by spraying the foliage of the deficient trees,[143] and also by injection of potassium salt solution or of solid into affected branches.[144,145] Injection of potassium salt solutions into leaf stalks has been used as a method of diagnosis for potassium deficiency, any deficiency being shown by a visible colour change round the injection site.[146,147] Another diagnostic method which has been proposed is the use of more sensitive indicator plants which would readily show visual signs of deficiency.[148] The Hoffer test for potassium deficiency by estimating the iron content of the nodes and internodes depends on the inverse relationship between the absorption of these two elements and applies only to maize. It has become obsolete since leaf symptoms are a better guide.[149,150]

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(v) Absorption of potassium by plants

There are a number of reviews of earlier work on the absorption of potassium by plants.[1-4] Plants differ widely in their ability to withdraw potassium from a given soil[5] and the absorption depends on such factors as the activity of the potassium ions, the pH and total salt concentration of the soil solution and the ionic activity of the root surface.[6] Since, as will be discussed later, absorption is dependent on the plant metabolism, temperature is an important factor, though light seems to be of secondary importance.[7] Fifty per cent. more potassium may be taken up by plants during a wet than during a dry season. The uptake is also directly proportional to the extent of root development.[8] Potassium may be transformed from an insoluble form in the clay mineral complex to a soluble, ionic form suitable for absorption by plants after hydrolysis by the soil water, the action of root secretions or by cation exchange with other cations in the soil water. These methods are, however, believed to be less important than direct cation exchange between root in contact with the potassium complex (contact exchange).[9-12] Root contact may not be necessary for all soils and species of plants.[13] The greater is the cation exchange capacity of the plant root colloid, the higher is the uptake of bivalent ions relative to univalent ions. Thus plants with a high exchange capacity will take up less potassium at the same soil level than plants with a low capacity and the former will in fact have a higher requirement for potassium than the latter. The cation exchange capacity of dicotyledonous plants is roughly double that of monocotyledons.[14] The nature of the predominant clay mineral has considerable influence on the absorption of potassium by plants.[15] Other factors of importance are the mean free energy change in the cation exchange against hydrogen ions, and the activities of the potassium and hydrogen ions.[16] When one half of the roots of a potato plant were placed in a solution deficient in potassium, the other half of the roots being supplied with potassium, unilateral deficiency symptoms developed in the plant, indicating that there is little transfer of potassium across the plant.[17,18] As rye plants age the potassium content decreases, the salt being said to be excreted through the roots.[19] Potassium may also be absorbed through the leaves, stems, branches or shoots[20] but absorption through the leaves only of sugar beet yields midget plants.[21] Absorption of potassium by excised roots increases as the roots expand, an effect attributed to the increasing protein content.[22] Uptake of potassium is correlated with both uptake of water and with sucrose content in excised pea roots.[23] Potassium salts tend to increase

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the outward diffusion of electrolytes from root preparations[24] as also does plasmolysis.[25] Potassium ions inhibit the uptake of rubidium or cæsium ions by discs of carrot tissue.[26]

The rate of uptake of potassium depends on the age of the plant and in general appears to be at a maximum during early growth before flowering.[27–33] More potassium may be absorbed during this period than is required for normal growth,[34] the element being translocated within the plant should the supply of potassium become restricted. In some species of plants, such as rice and other cereals, potassium appears to be absorbed continuously throughout the growth period,[35,36] although a very abrupt decrease in the rate of absorption of potassium has been found to occur in rice with age.[37] In some species of conifer,[38] hops[39] and brussels sprouts[40] the rate of potassium uptake is at a maximum during the middle period of growth. In sugar cane the rate of absorption is maximal between the sixth and the tenth months and thereafter almost ceases, potassium being supplied to the growing tips by translocation from maturing younger sections.[41,42] Although the curves for relative growth and for potassium content are roughly parallel, the intake of potassium is usually in advance of the total dry matter production.[43–45] Experiments with corn indicate that plants may be unable to obtain sufficient potassium from very dilute solutions even when these are renewed constantly.[46] An extensive investigation of the absorption of potassium ions by French prune trees grown in nutrient solution disclosed a correlation between the rate of absorption and temperature, the maximum rate being in the period June–July.[47]

The absorption rate varies not only with the species but also with the variety of plant, available potassium being taken up more rapidly by varieties which grow rapidly.[48] Although a high transpiration rate increases absorption, the increase is not proportional to the amount of water transpired.[49] Plants have been found to take up potassium just as readily at night as during the day.[50] The absorption of potassium by plants from soils in the course of the Neubauer test used for determining the available potassium of soils has been found to follow a simple empirical equation, but there is some doubt whether this equation would also apply to normal cropping.[51] It has been suggested that absorption of potassium by barley roots consists of two phases, a predominant one of undissociated salt absorption and a secondary one of ionic absorption by ion exchange in the root cells. The absorption curves show a periodicity attributed to the interference between absorption and swelling.[52] A sudden variation in the weight of the plant is found to coincide with a certain single point on the absorption curve.[53] The potassium absorption curves for sprouts and rye show a minimum absorption rate at about 4·5 days after sowing, the greater part of the potassium being assimilated in 5 to 12 days.[54]

A number of kinetic studies have been made of the absorption of potassium using the radioactive tracer techniques. It is found that with barley roots the rate of absorption increases rapidly as the concentration of potassium ion increases up to 0·005 N. but thereafter remains independent of concentration. The maximum rate of absorption is approximately $7·8 \times 10^{-7}$ milliequivalents of potassium per second per sq. cm. of root surface (1·71 milliequivalents per hr. per 100 g. fresh roots). Calculation shows that only 1 in 10^{8} of the ions striking the root surface is absorbed.[55] The time course of the absorption of potassium and chloride ions by wheat plants has been studied by analyses of root sap and it is found that the two ions do not accumulate at the same rate, the anion concentration slowly increasing over long periods while the cation concentration slowly decreases from a maximum value to approach equivalence with the anion.[56] The course of absorption of potassium salts by carrot root tissue could also be divided into two phases.[57] In certain cases the number of potassium ions entering the root may be eight times the number returning to the soil.[58] The rate of potassium absorption by red beet root tissue depends on the salt concentration inside the cells and is increased by washing with aerated distilled water.[59] Most of the potassium is taken up by irreversible absorption.[60] Studies of the competitive absorption of potassium and rubidium or sodium ions gave results consistent with the theory that absorption occurs through an intermediate labile complex of the ion with a metabolically produced carrier.[61]

When many species of plants are grown in constantly renewed nutrient solutions of different hydrogen ion concentrations, the absorption of potassium appears to be independent of the pH.[62] The pH of static nutrient solutions decreases at first to a minimum and then increases to a maximum above that of the original solution.[63] Pretreatment of roots with acid solutions causes the rate of potassium absorption to fall off rapidly below pH 6, and below pH 4·3 potassium is actually lost from the tissues. Small concentrations of calcium and lanthanum cause a stimulation of potassium absorption at pH between 2 and 6, and there is no loss from the tissues until below pH 2·5.[64] All these facts are in accordance with the theory of cation exchange with a metabolic carrier HR as described by the equation: $HR + K^{\cdot} = HK + H^{\cdot}$. The critical ratio of $K^{\cdot}$ to $H^{\cdot}$ in solutions is 17:1 and below this ratio potassium is lost from the roots, being absorbed at higher ratios.[65,66] The absorption of potassium appears to be favoured by illumination of the plants, suggesting a connection between absorption and photosynthesis.[67-69] Potassium uptake is lower in the absence of carbon dioxide even with illumination[70] and is increased if starch is present in the plant.[71] The absorption of potassium by corn roots is markedly reduced by low partial pressures of oxygen or high pressures of carbon dioxide.[72] Immersion of carrot, red beet tissue or barley roots in solutions of potassium chloride caused an increase in the oxygen uptake (salt respiration). This salt effect is maximal in chloride solutions of 0·01 M. and is completely inhibited by cyanide solutions as weak as 0·001 M.[73,75] Adsorption of potassium ions by barley roots is inhibited by most enzyme inhibitors.[76] Treatment of various root sections with 0·005 N. solutions of potassium bromide or potassium bicarbonate causes an increase in total organic acids present in the root, chiefly pyruvic, succinic, *trans*-aconitic, citric and malic acids.[77] It has been shown that the relation between the concentration inside the plant root and that of the surrounding solution can be described by the Donnan equilibrium. The concentration of potassium inside the root changes over the range 5·5 to 1 for a 100 to 1 change in the concentration of the outside solution.[78] The concentration of non-mobile anions in the cytoplasm of bean and maize roots is about 0·01 mol. per l. The uptake of potassium ions by bean root tissue is found to follow Fick's law of diffusion, the coefficient of diffusion being about one twentieth of the value for diffusion in free aqueous solution.[79] This diffusion is reversible, approximately the same amount of salt entering or leaving the tissue on reversing the conditions.[80] Ion absorption may also be regarded as an electrical phenomenon, for maximum potassium uptake occurs in eucalyptus seedlings when the inner plant tissues are 2·13 V. negative to the outer solution.[81]

Earlier work on the translocation of potassium in plants has been reviewed.[82] Redistribution of potassium ions inside the plant from leaves to fruits or seeds and from primary to secondary shoots has been established for many species.[83-86] By using ^{42}K as a radioactive tracer three stages have been distinguished between uptake of potassium and its appearance in the leaves of sunflowers: (1) an initial, rapid accumulation varying inversely with the salt concentration of the medium, this stage lasting three hours, (2) an apparent saturation occurring at about nine hours, and (3) a renewed absorption starting at seventeen hours and coinciding with symptoms of leaf damage due to excess of potassium.[87] Migration of potassium within a plant may be inhibited if the potassium content of the plant is lower or greater than an optimum value.[88] A high calcium content inside a plant will also hinder internal migration of potassium.[89,90] Potassium is, however, absorbed by plants from soil more rapidly than calcium.[91] Sodium does not appear to influence the movement of potassium inside plants.[92] The velocity of transport of potassium in the pedicels of *Bellis perennis* was greater than that of the other alkali ions.[93] The translocation of foliar-applied potassium in bean plants is markedly reduced as the temperature is lowered.[94]

The absorption of potassium by plants from soil is also influenced by the other anions and cations that may be present in the soil or be applied as fertilisers.[95] There is an optimum ratio of nitrogen, phosphorus and potash (N, P, K ratio) for each plant and this ratio may determine the uptake of the ions. There is evidence that potash is taken up by plants in satisfaction of their needs, so that if the supply of nitrogen (or phosphate) is deficient, only a small amount of potassium will be required for the reduced growth and thus the demands of the plant are reduced.[96-100] When citrus plants are grown in nutrient solutions in which the nitrate nitrogen is more than 100 times that normally adequate for growth, the leaves soon display the characteristic burn due to excess of potassium.[101] There is also a species effect, since addition of nitrogen fertilisers to soil causes increased potassium uptake by sugar cane but not by coffee. Addition of potassium salts to soil lowered the nitrogen and calcium uptake by coffee but did not affect phosphate uptake.[102] Sodium nitrate has a greater effect on potassium absorption by maize than has dried blood,[103] whereas in other trials the absorption of potassium by tobacco was enhanced by nitrate and decreased by ammonium salts.[104] There is a marked increase in the uptake of potassium by plants when calcium carbonate is added to the soil.[105-108] This may be due either to control of pH or to release of potassium from fixed forms, since the calcium level of the soil appears to have little influence on the uptake of potassium, although high soil levels of potassium do markedly reduce the uptake of calcium.[109-113] It has, however, been shown that a given concentration of calcium may exert either a depressing or a stimulating effect on the absorption of potassium, depending on the concentration of the latter ion in the external medium. It is suggested that the first action may be due to competition for a metabolically produced carrier, while the stimulating effect may be due to the function of calcium as a cofactor in the subsequent utilisation of potassium.[114] There may be an accumulation of calcium ions over potassium ions on the surface of roots. Thus with a calcium to potassium concentration ratio of 4 in the soil, the ratio on wheat roots is found to be 10 and on alfalfa roots 24.[115] Measurement of cationic activities by means of clay membrane electrodes also shows that many species of plants bind calcium more strongly to their roots than potassium.[116,117] More potassium than calcium is, however, taken up by the plants and the actual potassium to calcium ratio found inside the plant depends not only on the relative proportion of the soil exchange complex but also on the type of clay mineral. Thus much higher ratios of potassium to calcium ions are taken up from montmorillonite clays than from kaolinite clays. This phenomenon has been explained as a valence effect on the Donnan distribution of ions in a system of two colloidal phases of different ionic activities, but may be due to firmer binding of calcium by montmorillonite.[118] Calcium may be displaced from roots by solutions of salts of potassium and other alkali metals and this exchange does not seem to be affected by enzyme inhibitors.[119] Magnesium seems to behave towards potassium absorption in a very similar manner to calcium.[120-124] A higher level of exchangeable potassium in soil is required to decrease the absorption of magnesium as against calcium.[111] The so-called antagonism between iron and potassium, in that a high content of iron is associated with a low potassium content and vice

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versa, occurs in maize but not in wheat, barley, turnips or potatoes.[125] On the contrary, iron and potassium appear to be interrelated in the metabolism of the potato, the uptake and the translocation of either element being influenced by the level of supply of the other element.[126] There also appears to be some connection between the supply of potassium and uptake or mobility of manganese,[127] of copper[128-130] or of cobalt.[130] Excessive concentrations of sodium chloride in the irrigation water reduce the absorption of potassium by green beans.[131] In other instances, in experiments using cotton, sugar beet or wheat, addition of sodium salts to the soil increased the uptake of potassium, either by increasing the availability of the potassium or by increasing the root system of the plant.[132-134] Again, with peas grown in nutrient solutions, an inverse relation has been found between sodium and potassium.[135,136] The actual behaviour of any given plant depends on the level of available potassium among other factors. Sodium is absorbed against a greater concentration gradient than is potassium by sugar beet, a sodium–potassium concentration ratio of 1:10 in the soil being narrowed to 1:2 in the upper leaves.[137] Potassium accumulation by orange trees is retarded by boron deficiency.[138] Potassium and rubidium interfere with the absorption and utilisation of each other.[139,140]

The anion associated with potassium is found to have some effect on the uptake of the latter, since there is good evidence that more potassium is taken up by plants fertilised with the chloride than with the sulphate.[141-145] Young maize plants during the first three hours take up 3 times as much potassium as chloride ion from a solution of potassium chloride. Thereafter the uptakes of the two ions are more nearly equal.[146] Potassium chloride increases the ammonia uptake of beet seedlings, the effect being ascribed to the chloride ion.[147] On the other hand the potassium ion is believed to play an important part in nitrate absorption and metabolism.[148] Limiting the potassium supply of wheat tends to increase the total anion:cation ratio in the plant.[149] Addition of sodium silicate to a black clay soil increases the uptake of potassium by crops.[150]

The potassium content of sugar beet is found to depend on the night temperature.[151] Cultivation practices which tend to compact the soil reduce growth and decrease the content of potassium in the plants.[152] Such treatments as permanent grass, clover, annual clover crops or clean cultivation have a significant effect on the uptake of potassium by apple trees.[153] Fungicides, herbicides, and insecticides affect the uptake of potassium by conifer seedlings insofar as they affect the growth.[154] Certain sulphonamide drugs which were tested for their effect on the growth of rice also increased the potassium content.[155] Treatment of the roots of rice plants with hydrogen sulphide inhibited the uptake of potassium. Unilateral effects were again observed in that treatment of the roots of one side did not affect the uptake by the roots of the other side.[156]

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(vi) Physiological effects of potassium on plants

It has long been recognised that potassium fertilisation produces plants of greater strength or rigidity, but measurements of the cell walls and the lumina of *Dactylis glomerata* grown under various conditions show that in this species the increased rigidity is not due to anatomical strengthening,[1] and in fact, potassium seems to cause the cell walls to become thinner, while schlerenchyma and mechanical vascular tissue are better developed by poor potash supply.[2] The influence of potassium is most noticeable in fibre-forming plants such as flax, hemp, ramie, etc., where a good supply of the element is associated with swelling and increased thickness of the cell walls and a greater capacity to hold water.[3] The effects probably result from a primary lyotropic effect on the hydration of the cell walls.[4] The supply level of potash has no effect on the thickness of the seed coat of peas but does increase the toughness.[5] Through its action on the phytin of the seed coat,[6] potassium more than any other mineral ion reduces the time required to cook peas. Potassium ions have been found to reduce the motility of the stomata of leaves,[7] and applications of potash thus tend to reduce the drought resistance of plants.[8,9] The heat resistance of succulents such as cactus and aloe is improved by treatment with potassium chloride solution.[10] Potassium stimulates cell division[11] but a deficiency of potassium causes mitotic anomalies and especially hyperchromasia in the root tips of *Vicia faba*.[12] There is a positive correlation between potash supply and root-growth,[13] while the rooting of cuttings of *Phaseolus vulgaris*[14] and of tomato[15] is apparently promoted by potassium salts. Potassium salts in the nutrient solution increase the storage qualities of chicory.[16] Normal potash fertilisation is found to increase the resistance to injury by cold of pecans[17] and of winter wheat.[18] The effects of potassium salts on the electrical potential of plant cells and roots have been studied and the relative mobilities of the ions in the protoplasm calculated from the results.[19-21] The conductivity of potato tuber juice is positively correlated with the potassium content of the tubers.[22]

A number of investigators have developed the theory that the physiological importance of potassium is due to the presence of a radioactive isotope whose radiations stimulate biochemical processes.[23-27] It has been suggested that this radioactive effect may be combined with a photoelectric effect of potassium.[25] As experimental evidence in favour of this theory it has been shown that potassium salts enclosed in thin glass tubes stimulate the growth of plants[28,29] and that the kinetics of proteolytic enzymes are stimulated by radiation from radium,[23] while the percentage of seeds germinating appears to be increased by exposure to potassium salts.[30] It is, however, argued that the concentrations of radioactive isotope are too small to be of significance and experiments in which radium ores were added to soils in various proportions showed that the addition was detrimental rather than favourable to the yield of crops.[31]

It is now clearly established that potassium can help to combat many plant diseases.[32,33] Thus, potassium tends to increase the resistance of plants to attack by *Bacterium tumefaciens*,[34-36] *Bacterium carotovorum*,[35] and *Bacterium pruni*.[37] The fungal diseases cabbage clubroot[38] and black currant leaf-spot[39] appear to increase with potash fertilisation but most fungal infections are greatly diminished by increasing the potassium supply, so much so that such fertilisation is often recommended as a means of control. Excellent control is thus achieved of black heart in celery,[40] apple scab fungus (*Venturia inaequalis*)[41] rusts in garden beans[42] and in cotton,[43] fusarium wilt of cotton[44-48] and of tomatoes,[49] fusarium rot of narcissus[50] and squash,[51] mildews of grain crops due to *Erysiphe graminis*,[52-53] foot and root rot of wheat due to *Helminthosporium sativum*[54] and smut caused by *Urocystis tritici*.[55] The greatest concentrations of cucumber virus I in spinach were found after potash treatments which yielded the greatest growth[56] but potassium ions have been shown to be potent inhibitors of many viruses including tobacco mosaic in tobacco,[57,58] turnip virus 1 in tobacco[59] and spotted wilt virus in tomato.[60] Although a deficiency of potassium decreased the population build-up of aphids, *Macrosiphum pisi*, the deficient plants were more susceptible to attack by the aphids.[61]

Potassium has a favourable effect on the yield of seeds by plants[62-64] and the germination of the seeds of many species of plants is increased after treatment with solutions of potassium salts, of which the nitrate appears to be the most effective.[65-70] Marquis wheat is, however, indifferent to potassium nitrate[71] while kok-saghyz,[72] dandelion[72] and olive seeds[73] are adversely affected by treatment with solutions of potassium hydroxide. The potassium salt has not been found to penetrate through the seed coat and the stimulating effect of the salts cannot be correlated with entry into the seed.[74-76]

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(vii) Effects of potassium on plant metabolism

The general role of potassium in the metabolism of plants has recently been reviewed.[1] The respiration rate of barley leaves appears to be influenced by potassium in a complex manner. At high levels of potassium supply there is an inverse relationship between respiration rate and amount of potash supplied. At low supply levels, the relationship is positive. This positive relation appears to be due to the low carbohydrate concentration caused by the low potassium supply, for the relation becomes inverse when the carbo-

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hydrate in the leaves is increased.[2] An increase in respiration rate and respiratory coefficient with potassium deficiency has also been noted in the potato,[3] sugar cane,[4] onion[5] and flax.[6] The respiration rate of barley roots is increased by potassium chloride sorbed on cation exchange resins, but the type of resin is important.[7] Assimilation of carbon dioxide depends on potassium supply, the actual effect appearing to depend on the age of the plants. It is not clear whether this is a primary or a secondary effect on the amount of chlorophyll present in the leaves.[8-12] In several cases potassium has been shown to be positively correlated with photosynthesis.[13,14] Potassium was not found to affect photosynthesis in *Elodea* at low levels but did increase the rate of the dark reactions following bright illumination.[15] Both the potassium concentration and the pH of nutrient solutions were found to decrease in the light and increase in the dark, suggesting that illumination causes potassium to enter the cells and replace hydrogen ions.[16,17] It has been suggested that potassium acts by initiating the condensation of monoses to polyoses, thus reducing the concentration of monoses which acts as a brake on photosynthesis.[18] The concentration of reducing sugars certainly varies inversely with the potassium content of the plant, being high in cases of deficiency.[3,19-22] On the other hand, starch varies directly with the potassium content in a large number of species of plants.[23-29] Starch synthesis in radishes was checked when the potassium content of the nutrient solution was high, but was accelerated at lower contents.[30] Sucrose also increased with potassium supply in several species of plants, notably in sugar beet.[29,31-33] The synthesis of sucrose by invertase is accelerated in the presence of potassium ions.[34] In melons, however, potassium reduced the content of both hexose and sucrose, this effect being neutralised by boron.[35] Protein synthesis is also bound up with potassium supply, the element apparently being effective in the synthesis of proteins from α-amino acids.[36-42] Potassium ions have been shown to be necessary for the synthesis of glutathione.[43,44] In cases of potash deficiency, ammonia, amide and amino nitrogen accumulate, although the effects may depend on the level of nutrition.[45-48] Under the same conditions putrescine accumulates in barley.[49] It has been suggested that plants with a predominantly aldosugar content (glucose) require a high potassium content in order to utilise ammonia-nitrogen satisfactorily, whereas plants with predominantly ketosugar (fructose) are able to utilise ammonia-nitrogen even when deficient in potash.[50]

The effect of potassium on the enzymes present in living plants is not altogether clear. It has been established that potassium inhibits some enzymes[51] and activates others,[52] but in many cases the changes in activity observed during fertilisation treatments with potash appear to be normal responses to the overall growth of the plant rather than specific responses to potassium.[53,54] Often only one activity of an enzyme seems to be affected by potassium; thus the synthetic activity of invertase varies directly with potassium supply while the hydrolytic activity varies inversely, indicating that the reaction is stimulated in one direction and hindered in the other.[54,55] The content as well as the activity of many plant enzymes is increased in conditions of potassium deficiency. This applies not only to amylase, sucrase and glucosidases but also to catalase.[29,56-60] In general, the activities of the following enzymes have been found to be increased by potash deficiency: diastase,[3,53] invertase,[3] peroxidase,[3] ereptase,[3] amylase,[59,61] sucrase[59] glucosidase,[59] catalase (lettuce, cabbage,[59] maize[60]), catechol oxidase,[60] and transasminase.[60] An increase in the supply of potash, on the contrary, increases the activities of the following enzymes: catalase (cotton, wheat,[56] apple,[57] sugar[61]), maltase[61] and ereptase (sugar cane).[61] Potassium has no effect on phosphorylase *in vitro*.[28] Potassium salts increased the growth of *Avena* coleoptile, the effect being greatest when manganese salts were present.

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Inhibition of this effect by iodoacetate or malonate occurred only at low pH values.[62] Potassium salts caused considerable increases in the concentrations of pyruvic, succinic, aconitic, citric and malic acids formed in root sections of barley, soybean, squash etc.[63] The titratable organic acid of apples[64] and pineapples[65] was also correlated with the potassium content of the leaves. An adequate potash supply increases thiamine synthesis in pea and tobacco plants,[56] and the niacin content of oat tissue, although biotin and pantothenate were decreased.[67] The ascorbic acid content of many plants is also markedly increased by potassium.[68-71] Carotene and chlorophyll are influenced by the potassium supply, but the relationship is complex and also appears to depend on the nitrogen supply.[72-74] High rates of potash application are found to increase the content of oxalic acid in sugar beet,[75] Swiss chard[75] and tung[76] and the essential oil content of *Mentha piperita*,[77] but to decrease the alkaloid content of *Lupinus*[78] and belladonna.[79]

The anion associated with potassium appears to have some effect on the growth and metabolism of the plant, for area per leaf and leaf water content were increased by potassium chloride but not by potassium sulphate, whereas starch formation was increased by the sulphate but not by the chloride.[80] While the potassium ion tends to promote the synthetic processes, chloride ion tends to increase the opposing hydrolytic process.[81] Plants with high chloride and low potassium contents contain two to three times as much organic acids as normal plants.[82]

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3 POTASSIUM AND MARINE OR FRESHWATER ORGANISMS

Many marine organisms are able to accumulate high internal potassium contents from the surrounding sea water, which has a normal concentration between 0·040 and 0·046%. Algae seem to be most efficient at this concencentration process and a potassium content of 13·56% has been recorded for the Japanese seaweed, *Hizikia fusiforme*[1] although the content of most species of seaweed is closer to 3%.[2-4] *Valonia* from the Bermuda Islands was found to contain 2%.[5] Sponges varied from species to species, *Dysidea crawshayi* being an efficient accumulator of potassium.[6] Echinoderms and tunicates accumulate potassium to a much lower level, of the order of 0·05–0·07%.[7,8] The electric organ of *Electrophorus electricus* contains 0·68–0·76%.[9] The muscles of marine animals such as *Sepia* and *Octopus* contain almost twice the potassium content of those of a terrestial invertebrate such as *Helix pomatia*.[10] Among the fish, salmon and tuna contain 0·240–0·350%,[11] skipjack 0·165%.[12] The plasma potassium content of most species of freshwater animal is usually of a lower order although there may still have been considerable concentration from the lower potassium content of fresh water. Thus the plasma of *Anodonta cygnea* contains 0·0016% of potassium, that of *Lymnaea stagnalis* 0·008%, but the muscle juices of these species may contain much more.[13]

Many marine animals show a definite requirement for potassium.[14] In some cases this potassium may be replaced by rubidium,[15] but rubidium is harmful at high concentrations. It has been estimated that the limiting amount of potassium required for growth of *Nitzschia closterium* is $3{\cdot}1 \times 10^{-16}$ g. per diatom.[16] The uptake of potassium by the alga *Caulerpa prolifera* is dependent on the concentration of calcium in the water.[17] This is not, however, a general phenomenon since in many species of algae ions are absorbed independently of each other.[18,19] In *Valonia* the actual ratio between the internal concentrations of sodium and potassium depends on the concentration of potassium in the external solution and does not appear to depend on a Donnan equilibrium.[20] The potential across the cell wall of *Valonia* varies with the concentration of potassium provided this is above a certain critical value, but is independent below this value, suggesting that a change occurs in the diffusion of potassium ions through the cell wall at this critical concentration.[21] In the absence of photosynthesis no uptake of potassium occurs in *Valonia*.[22] The rate of exchange of potassium in *Ulva lactuca* is increased by both illumination and rise of temperature, all the potassium being exchangeable.[23] Iodoacetate causes a marked progressive loss of potassium and gain of sodium in *Ulva* in the dark but not when illuminated, suggesting that the uptake is dependent on the metabolic breakdown of phosphoglycerate.[24,25] In this alga two independent mechanisms seem to be required to explain the uptake and distribution of potassium and sodium.[26] The rates of uptake of both sodium and potassium by *Nitella flexilis* appear to follow an exponential law,[27] but the ions can be differentiated by their effects on the potential across the cell membrane.[28,29] *Nitella* chloroplasts show a selective permeability to potassium ions.[30] The majority of marine animals examined are found to be in osmotic equilibrium with sea water but ionic regulation is poor in the more simply organised animals, coelenterates, echinoderms, polychaetes, lamellibranchs and gastropods, whose body fluids contain low protein contents. Regulation is much more pronounced in crustacea and cephalopods, all of

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which contain the respiratory pigment haemocyanin and whose body fluids are relatively rich in protein.[31-34] The rate of exchange of ^{42}K in sticklebacks was 0·15 and 0·30 mM./kg./hr. in fresh and sea water respectively.[35] The rate of uptake of ions is extraordinarily rapid; thus in *Spirogyra* potassium may accumulate to twenty times the external concentration within one minute.[36] Changes in the uptake and loss of potassium commence within ten minutes of fertilisation of several species of sea urchin eggs.[37] The potassium content of the pearl oyster also increases during the reproductive season.[38] The potassium content of the heart muscle of the fish *Scorpaena porcus* increases under the influence of excess carbon dioxide in the surrounding sea water and decreases when the oxygen content is severely reduced.[39] A markedly uneven distribution of potassium is found in the electric organ of the thornback, *Raja clavata*, the electric platelets having a high and the surrounding connective jelly a low content.[40] The uptake of ions by freshwater animals has been studied using frogs, goldfish and the crab *Eriocheir.* Uptake in the last two animals is through the gills and appears to involve ion exchange.[41]

Potassium ions are quite toxic to *Hydra* and this toxicity is increased in the presence of low concentrations of calcium but counteracted by higher concentrations.[42] Cæsium can replace potassium almost completely and quantitatively as regards development of the eggs of *Arbacia* into blastulæ.[43] Potassium seems to be important for parthogenesis of *Asterias* eggs[44] and together with calcium for the maturation of the eggs of *Barnea candida.*[45] Injection of isotonic potassium chloride solution into the visceral cavity of *Mytilus* induces spawning.[46]

The potassium content of the urine of *Necturi* is very close to that of the plasma[47] whereas the content of the urine of *Lobius piscatorius* is much lower.[48] Potassium is the least effective alkali metal ion (cf. barium) in causing positive chemotropism in *Paramecium caudata.*[49] Potassium salts appear to increase the permeability of the skin of tadpoles.[50] Potassium and calcium ions are indispensable for the production of luminescence and pulsations in *Pelagia noctiluca,*[51] and for the maintenance of the ciliary movement of *Mytilus.*[52,53]

Addition of potassium chloride to sea water causes rhythmic contractions of the melanophore muscle of decapitated *Eledone moschata.*[54] The action of an increased concentration of potassium ions on echinoderm, molluscan or crustacean muscle is a sharp drop in muscle tone followed by a period of inhibition.[55] There are considerable differences between families and species as regards the sensitisation of muscles to potassium by various agents.[56,57] Potassium and calcium are the only two ions for which an optimum concentration can be found which renders the threshold excitation current a minimum, all other alkali ions causing an increase in the threshold value.[58] The potassium content of the muscle fibres of *Carcinus maenas* is more than four times the sodium content, which suggests that a 'sodium pump' may be operating as in vertebrate muscle.[59] On the actinozoa *Calliactis* and *Metridium* potassium produces a greatly prolonged contraction.[60] Potassium ions reduce the injury potential of snail muscle.[61] The pallor produced in trout by pressure, due to a concentration of melanophores, is attributed to the action on the skin of potassium released from the underlying muscles.[62]

Potassium has a negative ionotropic and chronotropic effect on selachian and teleostean hearts.[63,64] High concentrations of potassium arrest the heart of the mollusc, *Anodonta,* in systole[65] and cause a progressive slackening of the rhythm with a lowering of the diastolic tonus in the heart of the oyster.[66] Deoxycorticosterone increases the resistance to cold of the snail heart, apparently by decreasing the potassium content of the cells.[67] A suitable balance of potassium and magnesium ions can prolong automaticity of the snail heart, the pair being more effective than potassium and calcium.[68,69] The rate of oxygen uptake by heart muscle of molluscs is increased when potassium is increased relative to other alkali ions.[70]

The nerve fibres of the spider crab are freely permeable to potassium and impermeable to sodium, just as are vertebrate nerves.[71] Addition of potassium chloride to the medium surrounding a single lobster nerve fibre changes the response pattern from that of highly repetitive, non-accommodating fibres to that of accommodative, non-repetitive ones. High concentrations of potassium increased the excitation threshold, whereas lack of potassium ions caused conduction block.[72] The movement of potassium ions into and out of nerve fibres during activity has been studied by means of the radio-active tracer, ^{42}K, in the giant axons of *Sepia* and cephalopod fibres.[73] The passage of an impulse is associated with the inward movement of sodium and outward movement of potassium from the axon, these changes being reversed on recovery.[74] More than 90% of the contained potassium is exchangeable and thus ionised inside the fibre.[75] Measurement of the potassium flux in the presence of electric currents through the axon wall indicates that the steady outward current associated with the depolarisation of nerve fibres is carried mainly by potassium ions leaving the axon.[76] The sodium and potassium contents of *Sepia* axon are 40 and 325 mM./kg. respectively (0·092 and 1·3%), the corresponding figures for the giant fibres of *Loligo forbesi* being 46 and 323 mM./kg. During stimulation of *Sepia* axons there is a net entry of $3{\cdot}8 \times 10^{-12}$ moles Na/cm.^{2}/impulse and a net loss of $3{\cdot}6 \times 10^{-12}$ moles K/cm.^{2}/impulse.[77] For crab nerve a potassium efflux of 3×10^{-9} moles per impulse per nerve has been measured.[78] This is of the same order as that of the giant squid axon when both are expressed per unit area, but active reabsorption occurs during recovery only in the crab nerve.[79] An increase of concentration of potassium in the surrounding solution depresses the impedance change more than the spike potential in the giant squid axon.[80]

Potassium ions are partly responsible for the potential difference existing across the protoplasm of *Halicystis osterhouti* and *Halicystis ovalis*. *H. ovalis* has a higher concentration of potassium in its cell sap and accordingly a higher potential, 79·7 mV. as against 68·4 mV. for *H. osterhouti*.[81] From the effects on the potential in *Valonia macrophysa* of changes in external potassium concentration it has been possible to deduce the relative mobilities of potassium, sodium and chloride ions in the outer protoplasmic layer of the cell.[82]

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4 POTASSIUM AND INVERTEBRATES

(i) Insects

The coelomic fluids of many species of insects have been analysed for sodium and potassium by micro-methods. It is found that vegetarian insects have a high potassium, low sodium, content while the reverse is true for carnivorous or bloodsucking insects.[1,2] No valid statistical difference has been found between the whole body potassium contents of *Culex tarsalis* and *Culex stigmatosoma.*[3] *Drosophila* contains 0·45% of potassium and it is calculated that the radiation from the associated natural radioactive isotope, ^{40}K, is only 4×10^{-5} of the dose required to produce mutations.[4]

The toxicity of potassium ions to *Drosophila* is intermediate between that of lithium and sodium ions at high concentrations.[5] A mortality of 50% was caused by exposure of larvae of *Chrysomyia megacephala* to 2·5% potassium hydroxide solution for 24 hr.[6] Silkworm eggs were all killed by exposure for 60 min. to 1% caustic potash, although 15 min. exposure had no effect on hatchability.[7] Potassium chloride used as fertiliser had no effect on bees by direct contact but caused 10% mortality on ingestion.[3] An insecticide-resistant strain of house flies was more susceptible to potassium bromide than a susceptible strain and potassium chloride gave complete protection in mixtures of the chloride and bromide.[9]

There was a positive correlation between the population of the two-spotted spider mite, *Tetranychus himaculatus*, and the supply of potassium in the nutrient solutions supplying tomato[10] and cucumber[11] plants on which the mites were reared. Potassium enters the body of mosquito larvae via the anal gills, is absorbed in the rectum and excreted by the Malpighian tubules.[12] Potassium ions do not compete with sodium ions in this process.[13] The concentration of potassium in the haemolymph of *Rhodnius* can be increased ten-fold by feeding potassium chloride without harm to the insect. The Malpighian tubules can secrete a urine richer in potassium than the haemolymph and there is evidence of subsequent re-absorption of sodium and water but not of potassium.[14] A similar mechanism appears to hold for the stick insect, *Dixippus morosus*,[15] and for a number of other species. Measurements of the potentials across the wall of the tubule indicate active secretion of potassium and passive excretion of sodium.[16] During pupation of the silkworm, *Bombyx mori*, there are changes in the distribution of potassium, a considerable proportion being transferred to the silk gland.[17]

Potassium has a toxic action on the insect heart if present in excess, causing arrest in systole.[18] Normal concentrations increase the tonus and frequency but decrease the amplitude of the dorsal vessel.[19] Potassium is able to counteract the toxic action of barium ions provided calcium is present but not if it is absent.[20] To maintain a normal beat a ratio of sodium to potassium concentrations of 3:1 is required but no appreciable effect was observed in the moth, *Samia walkeri*, when this ratio was varied between 34:1 and 1:13·8.[21]

Both the nerve axons and muscle fibres of insects are depolarised by high concentrations of potassium ions in the same manner as vertebrate and crusta-

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cean nerves.[22] The insect haemolymph normally contains a sufficiently high potassium concentration to depolarise crustacean fibres and the greater resistance of insect nerves is attributed to the protection of the nerve sheath which is an effective barrier to diffusion of potassium ions. Action potentials of insect nerves were maintained unchanged for hours in the presence of high external potassium concentrations but were rapidly blocked on injection of potassium salt solutions.[23] Calcium ions appear to antagonise the blocking action of high concentrations of potassium ions.[24] In contradistinction to the effect on vertebrate and crustacean nerves, increased concentrations of carbon dioxide increase the excitability of insect nerve, possibly by increasing transport of potassium out of the nerve.[25] Potassium chloride acts as a stimulus at concentrations greater than 3×10^{-3} M. on an isolated ganglion-muscle preparation of *Dytiscus marginalis*.[26] The normal ratio of sodium to potassium in the haemolymph of the African migratory locust is about 5:1 but the potassium content is readily decreased by as much as 50% of its normal value by starvation. Such a low potassium level is an essential condition for the maintenance of the marching state of hoppers.[27] The optimum ratio of potassium to calcium ions for maintenance of the tonus of fore-gut muscles of *Dytiscus marginalis* is 0·4.[28]

(ii) Other invertebrates

The potassium content of fresh muscle of *Helix pomatia* is: heart 0·311, foot 0·312 and columellar 0·364%.[29] The changes in tone of the *Helix* crop when the potassium concentration is varied resemble closely those occurring in vertebrate smooth muscle under similar conditions.[30] When increasing concentrations of potassium chloride are applied to the foot of a snail, the chronaxia at first decreases to a minimum and then increases beyond the normal value.[31]

Potassium chloride caused marked excitation of the nerve cord of the earthworm.[32] The effect has been studied of a number of inorganic salts, including potassium salts, on the photic orientation of the worm *Allolobophora foetida*. Potassium sulphate in general causes a weakening of the orienting function both of the ventral nerve cord and of the brain.[33] Application of potassium iodide solution greatly reduced attack by the eelworm, *Meloidogyne hapla*, on tomato plants grown in infested soil provided that the soil did not contain material from old infected roots.[34] The potassium content of *Ascaris lumbricoides* varies considerably with the composition of the external medium.[35]

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5 POTASSIUM AND VERTEBRATES

There have been a number of reviews of the literature on the importance of potassium to the health and well-being of mammals. Earlier reviews, previous to the 1939–45 war, tend to be rather general.[1-5] Excellent reviews are available of recent work on more specialised topics; thus, potassium as a pharmacological sensitiser,[6,7] its clinical importance,[8] its role in physiological and pathological processes,[9,10] its importance in cell physiology,[11] the 'biological antagonism' of sodium and potassium,[12,13] and the relation of potassium to hormones,[14] to normal metabolism,[15-17] and to abnormal metabolism in disease.[18]

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(i) Occurrence and distribution

There are a number of recent reviews on the determination of potassium in animal tissues.[1-3] Potassium may be determined in tissues either by aqueous extraction followed by the cerous sulphate method,[4] or by ashing the tissue, precipitation of the double salt potassium silver cobaltinitrite and titration by thiocyanate of the silver contained in the precipitate.[5,6] A useful method has been developed for determining potassium on a semi-micro scale, over the range 0·07–0·2 mg., which enables the potassium content of blood sera to be determined accurately on a 0·5 ml. sample.[7] In the most recent methods potassium is transferred from the tissue to aqueous solution either by aqueous extraction[8] or by electrolysis[9] and determined by flame spectrophotometry, usually abbreviated to flame photometry.

Reviews also exist of the recent literature on the general distribution of potassium in animal organisms,[10-12] the equilibrium between cellular and extracellular potassium,[13] the pathology of abnormal distribution[14] and the use of potassium salts in the therapy of such pathological states.[15,16] The normal distribution of potassium in the tissues and organs of animals is given in Table III.

TABLE III.- DISTRIBUTION OF POTASSIUM IN ANIMALS

Tissue	Species	Potassium per cent.	Ref.
Whole body	Rat	0·206(at birth)	17
Whole body	Rat	0·260	18
Whole body	Rat	0·321(fat-free basis)	18
Intracellular	Dog	0·460(of cell water)	19
Intracellular	Chick	0·560(of cell water)	37
Brain	Rabbit	0·360–0·400	20
Bile	Dog	0·021–0·056	21
Bile	Dog	0·032	36
Blood, plasma	Rabbit	0·0168	20
Blood, plasma	Rabbit	0·0146	22
Blood, plasma	Cow	0·049 (0·0277–0·0786)	23
Blood, plasma	Cow	0·004	24
Blood, plasma	Elephant seal	0·018	25
Blood, plasma	Rabbit	0·018	26,38
Blood, plasma	Guinea pig	0·0172	26
Blood, plasma	Rat	0·0168	26
Blood, plasma	Dog	0·0233	27
Blood, serum	Horse	0·0172 (0·0160–0·0182)	28
Blood, serum	Dog	0·0237±0·004	29
Blood, serum	Rabbit	0·0176	30
Blood, serum	Goat	0·0141	31
Blood, serum	Chick	0·028±0·005	37
Blood erythrocytes	Elephant seal	0·0272	25
Blood erythrocytes	Dog	0·0436±0·010	29
Blood erythrocytes	Sheep	0·096–0·376	32
Blood erythrocytes	Sheep	0·068–0·280	33
Cerebrospinal fluid	Horse	0·0127 (0·0107–0·0142)	28
Egg	Hen	0·107	34
Eye, vitreous humor	Rabbit	0·484	35

continued on following page

TABLE III.- continued

Tissue	Species	Potassium per cent.	Ref.
Gastric juice, fasting	Dog	0·033	36
Gastric juice, after meal	Dog	0·029	36
Intestinal juice	Dog	0·086	36
Liver	Rat	0·360±0·023	40
Liver	Guinea pig	0·280±0·017	40
Lymph	Rabbit	0·0130	42
Kidney	Rat	0·316±0·025	40
Kidney	Guinea pig	0·242±0·023	40
Milk	Mare	0·049	41
Milk	Cow	0·136–0·179	44
Muscle, white	Rabbit	0·369	26
Muscle, red	Rabbit	0·328	26
Muscle	Chicken	0·182±0·020	37
Muscle	Rat	0·417±0·009	40
Muscle	Guinea pig	0·356±0·009	40
Muscle thigh	Guinea pig	0·506±0·610	41
Muscle intestine	Guinea pig	0·249–0·267	41
Muscle heart	Guinea pig	0·388–0·415	41
Muscle heart	Guinea pig	0·38	39
Muscle heart	Dog	0·38	39
Muscle heart	Rat	0·36	39
Muscle, auricles	Rabbit	0·191	38
Muscles, ventricles	Rabbit	0·262	38
Pancreatic juice	Dog	0·041	37
Seminal plasma	Boar	0·215	45
Seminal plasma	Bull	0·172	46
Skin, whole	Guinea pig	0·440	47
Skin, epidermis	Guinea pig	0·607	47
Skin, cutis	Guinea pig	0·310	47

The changes undergone in the potassium content of tissues have been studied by measuring the content of various tissues of rat, guinea pig and rabbit after storage for various periods of time under different conditions.[48] The potassium content of animals varies with age, usually increasing from birth to a maximum at about ten days and decreasing thereafter throughout the life of the animal. This applies not only to the whole carcass[17] but also to specific organs and tissues.[49-51] It has been found that in rats, rabbits, cats and pigs there is more sodium than potassium in the body at birth, but that the sodium content rapidly decreases with age while that of potassium rises until the amount of the latter element is almost twice that of sodium.[52] Different tissues behave in different ways; thus the potassium content of the vitreous humor of the ox changes very little with age while the content of the aqueous humor changes much more than does that of the serum as the animals become older.[53] The potassium:calcium ratio also varies with age and seems to be high when the growth rate is high.[54-56]

Potassium appears to occur in the largest amounts in those tissues which are most active physiologically, such as the pancreas, salivary glands, liver etc. Potassium is more abundant in the female ovum than in the male spermatozoon[57] although it does occur in the latter.[58] In the adrenals of monkeys potassium is primarily located between the fascicular and the glomerular zones.[59] The potassium contents of the sera of a number of species of wild mammals varied between 0·019 and 0·0354%, the extreme values for whole blood being 0·029 and 0·117%.[60] The potassium content of the blood cells is much higher than that of the surrounding plasma. Common animals appear to fall into two groups, the first comprising man, bat, rat and horse, in which the ratio between the cell and plasma contents is 27±4, while in the second group, sheep, ox, cat and dog, this ratio is 6±4.[61] The potassium content of the plasma varies during egg production in birds[62] and also during menstruation.[63] The blood potassium content varies from day to day in dogs on a normal meat diet but is more or less constant during starvation.[64] There was no significant difference between the mean blood potassium contents of cock and hen turkeys.[65] The potassium content of the milk of cows is much higher at the beginning of lactation and tends to fall with time.[66,67] The normal endolymph of the labyrinthine fluid of guinea pigs contains 30 times as much potassium as the perilymph.[68]

There appears to be some connection between the heat regulation of the body and the potassium content of the blood plasma, though this connection is obscure. Thus, in a group of male rabbits the blood-potassium was found to be high in winter (0·022–0·023%) and low in summer (0·014–0·015%).[69] Direct sunlight on the skin of dogs caused a slight rise in blood potassium.[70] Natural hibernation in groundhogs (*Marmota mona*),[71] as well as artificial hibernation in rats induced by chilling and partial anoxia,[72] is accompanied by an increase in plasma potassium, but if the artificial hibernation is induced by drugs such as chlorpromazine, pethidine or promethazine there may be a large decrease in the plasma potassium content.[73-75] Fatal hyperthermia, produced either by external heat or by drugs, resulted in high serum-potassium contents while large quantities of potassium were extracted from the muscles.[76,77] There is an increase in the potassium content of the blood serum as a result of anaphylactic shock,[78] after oedema of the rear limbs[79] or following acute respiratory acidosis.[80] The potassium content of the muscles of dogs increased during parathyroid tetany but not after poisoning with guanidine,[81] while there is evidence that a potassium deficiency of the intestinal cells may contribute to, if not cause, paralytic ileus.[82] Hypoxia produced by decompression causes a marked decrease in the plasma-potassium concentration[83] as does anaesthesia by narcotics.[84,85]

The normal distribution of potassium in man is given in Table IV.

The average potassium content of the body calculated from measurements of the natural radioactivity agrees well with figures obtained by chemical analysis.[86] Determinations of the exchangeable potassium by injection of ^{42}K indicates that 7–25% of the total body potassium is non-exchangeable.[87,88] The references in Table IV are arranged in date order for each tissue. For each tissue or organ there is a range of variation which is larger than the range of accuracy of the method of analysis. Earlier analyses would be carried out by chemical methods but latterly more refined physical methods have been adopted, such as flame spectrophotometry[168] and electrodialysis.[134,137,163] In the case of some tissues the method of extraction or of preparation is extremely important. Thus since blood cells contain about 10 times as much

TABLE IV.- DISTRIBUTION OF POTASSIUM IN MAN

Tissue	Potassium per cent.	Method	Ref.
Whole body	0·136–0·284	Chemical analysis	86
Whole body	0·21±0·02	γ-ray emission	87
Whole body	0·17–0·24	γ-ray emission	88
Intracellular	0·196 (0·160–0·224)	Isotope dilution	89
Exchangeable	0·15–0·21	γ-ray emission	88
Exchangeable	0·180	Isotope dilution	90
Exchangeable	0·126		91
Bone	0·104		92
Blister fluid	0·0198–0·0390		93
Blister fluid	0·0169		94
Blister fluid	0·01373		95
Blood, whole	0·1938	Chemical analysis	96
Blood, whole	0·182 (0·160–0·212)		97
Blood, whole	0·166±0·021 (children)	Flame photometer	98
Blood, plasma	0·0265	Chemical analysis	96
Blood, plasma	0·022	Chemical analysis	27
Blood, plasma	0·0148–0·212		99
Blood, plasma	0·0195		100
Blood, plasma	0·145		101
Blood, plasma	0·0214 (0·174–0·0241)		102
Blood, plasma	0·0198	Chemical analysis	103
Blood, plasma	0·021(children)	Flame photometer	104
Blood, serum	0·020	Chemical analysis	105
Blood, serum	0·0227–0·0388	Chemical analysis	106
Blood, serum	0·018–0·022	Chemical analysis	107
Blood, serum	0·0208		108
Blood, serum	0·0207 (0·018–0·024)		109
Blood, serum	0·01797		110
Blood, serum	0·0233 (0·018–0·0535)	Chemical analysis	111
Blood, serum	0·02434		112
Blood, serum	0·020–0·034	Chemical analysis	113
Blood, serum	0·0192		114
Blood, serum	0·020 (0·0180–0·022)		115
Blood, serum	0·020–0·030		116
Blood, serum	0·0194–0·0218		117
Blood, serum	0·0193		118
Blood, serum	0·0193 (0·018–0·0206)	Chemical analysis	7
Blood, serum	0·01847 (0·0165–0·0210)	Chemical analysis	119
Blood, serum	0·01655± 0·00037		120
Blood, serum	0·0188± 0·00030		121

continued on following page

TABLE IV.- continued

Tissue	Potassium per cent.	Method	Ref.
Blood, serum	0·016–0·022		122
Blood, serum	0·0166± 0·00088		123
Blood, serum	0·02047		95
Blood, serum	0·019		124
Blood, serum	0·0175		125
Blood, serum	0·0188 (0·0156–0·0220)	Flame photometry	126
Blood, serum	0·020–0·021		127
Blood, serum	0·0199± 0·00205	Flame photometry	128
Blood, serum	0·0175–0·0195	Chemical analysis	129
Blood, serum	0·016–0·018		130
Blood, serum	0·0176	Flame photometry	131
Blood, serum	0·0172 (0·0156–0·0188)	Flame photometry	132
Blood, serum	0·0215 (0·01725–0·02505)		133
Blood, serum	0·0204	Electrodialysis	134
Blood, serum	0·018–0·022		135
Blood, serum	0·016–0·022	Flame photometry	136
Blood, serum	0·0196–0·0256	Electrodialysis	137
Blood, serum	0·0246± 0·004	Flame photometry	98
Blood, erythrocytes	0·4227		118
Blood, erythrocytes	0·3868		100
Blood, erythrocytes	0·506		102
Blood, erythrocytes	0·475	Chemical analysis	103
Blood, erythrocytes	0·3968 (0·374–0·463)		97
Blood, erythrocytes	0·3780	Flame photometry	138
Cerebrospinal fluid	0·0131	Chemical analysis	139
Cerebrospinal fluid	0·0155–0·0195	Chemical analysis	140
Cerebrospinal fluid	0·012	Chemical analysis	141
Cerebrospinal fluid	0·0117	Chemical analysis	142
Cerebrospinal fluid	0·010–0·018		143
Cerebrospinal fluid	0·010–0·016		144

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TABLE IV.- continued

Tissue	Potassium per cent.	Method	Ref.
Cerebrospinal fluid	0·011–0·015		127
Cerebrospinal fluid	0·0118 (children)	Flame photometry	104
Cerebrospinal fluid	0·0122–0·0127		145
Cerebrospinal fluid	0·01284 (0·0062–0·0330)		146
Gastric juice	0·0684 (0·05359–0·09957)		147
Gastric juice	0·070–0·0746		148
Gastric juice	0·0484 (0·0254–0·0664)	Flame photometry	149
Liver	0·225–0·300	Chemical analysis	86
Milk	0·052–0·112	Chemical analysis	150
Muscle	0·289	Chemical analysis	151
Muscle	0·28	Chemical analysis	5
Muscle	0·29–0·37	Chemical analysis	6
Muscle	0·240–0·608		152
Muscle	0·376±0·024		153
Eye, aqueous humor	0·309		154
Eye, vitreous humor	0·0186		155
Placenta	0·209	Chemical analysis	156
Pleural discharge	0·025–0·035	Chemical analysis	157
Pleural discharge	0·0226	Chemical analysis	96
Saliva	0·031–0·131		158
Saliva	0·0788± 0·0156		159
Synovial fluid	0·016±0·001		160
Skin	0·200–0·300 (dry weight)	Chemical analysis	161
Skin	0·322		162
Skin	0·0564± 0·0024	Iontophoresis	163
Sweat	0·0232		164
Spleen	0·295–0·342	Chemical analysis	86
Tooth, enamel	0·3		165
Uterus	0·188		166
Uterus	0·138–0·248		167

potassium as the surrounding serum, the greatest care must be taken to avoid damage to the cells when separating them from serum.[105] There is a progressive leakage of potassium from the cells on standing, the serum content rising

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about threefold during 24hr. storage at 4°C.[169-171] This leakage also occurs post mortem in the body so that for accurate results samples must be collected within ten minutes of death.[136] Venous plasma contained more potassium than did arterial blood after the ingestion of glucose but the contents were about the same under fasting conditions.[99] The content of capillary blood serum was greater than that of venous blood.[129] The serum potassium concentration varies during the menstrual cycle, reaching a peak at the time of ovulation[172] and it decreases markedly during the later stages of pregnancy.[103,173] The content of the placental serum is almost double that of the maternal serum.[108] An inverse relationship has been observed between blood pH and potassium concentration.[174,175] The serum potassium content increases in winter and decreases in summer while the serum calcium changes in the reverse manner, so that the potassium:calcium ratio changes much more strikingly with the season[176,177] and in fact with the time of day.[178,179] The serum potassium content is increased when the body is chilled by exposure to low temperatures.[180,181] Scorpion toxin increases the serum potassium concentration through its action on the permeability of the red cells.[182] Although the cerebrospinal fluid is a dialysate of blood plasma, the potassium concentration is only about 60% of that of plasma,[141,142] and remains virtually constant with changing serum potassium concentration.[183] The potassium concentration of aqueous humor is increased by light[186] and by an increase in the plasma concentration following injection of potassium salts. Acidosis appears to impede the transfer of potassium from plasma to humor.[187] Potassium appears to be interchangeable with sodium in bone as mixed alkali calcium carbonate.[188] Attempts have been made to locate the exact distribution of potassium in the various layers and cells of skin by histochemical tests.[189]

The potassium content of the human foetus rises steadily from the 4th month to birth from 0·16 to 0·20%[190,191] reaches a maximum between one and three days after birth and then falls gradually to the adult level.[192,193] The total potassium in the human body at different ages can be expressed by a simple equation.[194] There is a tendency for the blood plasma concentration to increase with age but the correlation is not statistically significant. The potassium content of red cells does not vary with age.[195,196]

The blood-potassium concentration is markedly increased by fatigue[197] and in shock caused by anaphylaxis,[198] histamine injection[199] or by other means.[200] The exchangeable potassium of the body is not affected by disease,[201] neither is the content of the red cells greatly affected.[118,138] In cases of sickle cell anaemia the cells lose potassium rapidly when the oxygen tension is low.[202] The serum-potassium concentration is reduced in some infectious diseases[203] and increased in others.[204] In advanced diabetes the plasma potassium content is increased, often considerably,[205] but in diabetic coma the blood potassium falls below normal.[206] A potassium deficiency in the patient may make adequate control of the diabetes difficult.[207] Administration of insulin or of glucose tends to reduce the serum potassium content.[99,208,209] The potassium concentration of the serum may be rapidly reduced to low levels by persistent vomiting due to intestinal obstruction.[210,211] Similar losses, imperfectly understood, occur after surgery.[212] The potassium:calcium ratio may often be a more sensitive diagnostic index of disease, being increased in cases of bronchial asthma, hypertonicity and epilepsy,[109-211,213] and in circulatory diseases with cardiac insufficiency.[214] The potassium contents of skeletal and cardiac muscle, of liver and of kidney are considerably reduced in subjects dying of congestive heart failure.[215] No relation has been found between the potassium concentration of the cerebrospinal fluid and neurologic or psychiatric diseases.[146] Blood serum potassium is increased in nephritis and in muscle disease such as tetany[107] or myocardial infarct.[135] The serum potassium content falls in familial periodic paralysis and attacks can be prevented by injection of potassium salts.[216] The potassium content of the blood serum is considerably increased in cases of carcinoma[113,217,218] but the ratios of concentrations between potassium and other cations are not significantly different from normal.[219] The potassium content of many forms of carcinoma is greatly increased often being double that of normal tissue.[220-223] The potassium concentration of the bone marrow is raised in carcinoma as in periods of growth activity again to at least double that normal in adults.[224] In both Rous and Jenson sarcoma[225,226] and also in acute leukemia[227] the potassium content of the blood and of the tumour tissue is abnormally low.

The natural radioactivity of the human body has been measured by several techniques and is deemed to be due almost entirely to ^{40}K; this evidence indicates that the body contains about 150 g. of potassium.[228,229] Measurements with a mass spectrograph of the abundance ratios of the principal isotopes of potassium indicate that there is enrichment to the extent of about 1% of ^{39}K over ^{41}K in carcinoma,[230] sarcoma[231] and in the auricle and small intestine,[232] while the bone marrow shows a corresponding increase of the heavier isotope, ^{41}K. Significant separation of the radioactive isotope ^{40}K could not, however, be demonstrated by means of a Geiger counter.[233,234] Rubidium-86 has been used to trace the movement through the body of potassium over long periods of time, since this element is believed to behave very like potassium. One half of the rubidium was excreted in the urine in 58–188 days.[235] The radioactive ^{42}K isotope has been used much more widely for studies of the distribution and movement of potassium in the body.[236,237] The injected isotope disappears from the body in five exponential stages, the first being a rapid transfer through the capillaries, the second uptake by the kidneys followed by redistribution in other organs, intestine, liver, skin; the third and fourth stages represent movement into muscle, the fifth stage elimination from the body.[239,240] Muscles depleted of potassium by dieting may be rapidly restored after administration of potassium salts.[241] There is a much more rapid dynamic exchange between intra- and extra-cellular potassium in other organs,[243] although potassium leaves the cells in bulk only if it can be excreted.[243] There is a rapid loss of exchangeable potassium on starvation.[244] The maximum rate of diffusion of potassium into tissues in patients given potassium salts intravenously was 12·9 mg./min.[245]

There have been many claims that not all the potassium of biological fluids is dialysable or ultrafiltrable. Thus about 18% of the potassium contained in cow's milk is stated to be non-filtrable through collodion membranes,[246] while a much greater percentage of the potassium of human milk is said to be unionised.[150] Only 67% of the potassium of the vitreous humor is ultrafiltrable.[247] Although the potassium of the blood serum is claimed to be completely removed by ultrafiltration,[248,249] a certain percentage of this potassium is found to migrate to the anode together with the albumin.[250,251] Not all the potassium of muscle is extractable by mincing with Ringer solution and the proportion unextracted increases in muscle poisoned with guanidine.[252]

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(ii) Growth requirements

The dietary requirements of potassium for normal healthy growth in small mammals appears to be much the same; rat, dog or pig require about 0·15,[1] chick 0·13,[2] 0·20–0·24,[3] 0·23–0·40,[4] pig 0·15,[5] 0·12%[6] of the diet. There is evidence that the actual level depends on the ratio of sodium to potassium in the diet;[1] thus for the rat a potassium supply of 0·18% is adequate in the presence of 0·1% of sodium but this may be reduced to 0·15% if the sodium is increased to 1% of the diet.[7] The actual composition of the diet in terms of fat and protein also influences the requirement.[8] The effects of potassium salts in the diet on the health of ruminants have been critically reviewed.[9] The temporary replacement of dietary sodium by the equivalent quantity of potassium gave slightly increased milk yields from cows with a normal blood Na:K ratio but not from those with a low ratio.[10] The calcium:potassium ratio is regarded as important in the diet of pigs.[11] Addition of a small quantity of potassium iodide to the diet of mares in gestation appeared to result in the foaling of stronger and healthier colts.[12] The minimum potassium requirement for human nutrition is 3·3 g. calculated on a diet of 2500 g.-cal. or 5 g. per 100 g. protein.[13] Additional supplies of potassium are required by the body after surgery[14] and menus have been prepared to give various levels of potassium.[15]

(iii) Potassium deficiency

The biochemical, physiological and pathological aspects of potassium deficiency in animals[16] and in man[17-20] have recently been reviewed.

Potassium supply becomes deficient for rats when it is less than about 0·01% of the diet, and death usually occurs in 12–24 days among young rats although older rats may survive a little longer.[21-24] The heart always stops in systole.[22] At this supply level the sparing action of sodium does not seem to occur.[7] Sexual function is usually impaired and the water intake is reduced. The potassium content of the muscles and in particular the heart is markedly lowered,[23] which leads to widespread oedema and lesions in the heart and viscera.[24] Necrosis and scarring of the myocardial fibres together with necrosis of the renal tubular epithelium are typical symptoms of potassium deficiency.[25-28] Muscular but not cardiac lesions are very rapidly repaired even by a single day of potassium therapy.[29] Potassium deficiency in the diet of female rats appeared to result in myocarditis in their offspring.[30] Simultaneous magnesium and potassium deficiencies produced symptoms very similar to those produced by potassium deficiency alone.[31] There is a large reduction in the potassium content of the whole body of rats on a deficient diet which can be largely attributed to changes in the muscle potassium[32] which may in fact be reduced to 40% of its normal value with no effect on the rate of oxygen consumption.[33] Intestinal stasis is produced in rats when both potassium and calcium intakes are low.[1,34] Potassium deficiency is associated with a rise in the pH of the gastric juices of rats.[35] Sodium chloride may become lethally toxic to protein-depleted rats maintained on a potassium deficient diet.[36,37] The association of potassium and amino nitrogen assimilation has been clearly demonstrated in rats.[38,39] The muscles from potassium-depleted rats show a large increase in *L*(+)lysine which appears to replace potassium in the muscle so as to maintain the total cation concentration constant.[40] The condition among horses known as 'going sour'[41] and that of 'pullet disease'[42] among chickens have both been shown to be simple cases of potassium deficiency.

Experimental potassium depletion in man caused marked changes in the serum potassium content and an extracellular alkalosis without the development of severe clinical symptoms,[43] the chief symptoms being thirst, haemoconcentration and mental confusion.[44] Such a state of deficiency has been maintained for 65 days without harm.[45] Diets restricted in potassium have been produced for the treatment of Addison's disease.[46] Accidental potassium deficiency may be produced through the over-use of laxatives,[47] through losses in saliva among patients unable to swallow this, e.g. because of burns of the oesophagus or pharyngeal paralysis,[48] through losses of gastro-intestinal secretions following surgery,[49] and after taking such drugs as adrenocorticotropin, cortisone derivatives, or *p*-aminosalicylic acid.[50] Potassium deficiency, particularly if accompanied by calcium deficiency, may lead to intestinal stasis which if severe may become a paralytic ileus.[34,51] The central nervous system changes occurring during starvation may be caused by potassium deficiency,[52] as may congestive heart failure.[53] Solutions of potassium salts varying in phosphate content have been prepared for the relief of potassium deficiency.[54]

(iv) Toxicity of potassium

The pharmacology and toxicology of potassium salts have been reviewed recently.[55-58] The following doses of potassium chloride were toxic on intraperitoneal injection: rabbit, 0·575 g./kg. body weight, rapidly fatal;[59] mice, 0·637 mg./g. body weight, 50% mortality;[60,61] toad, 0·8 mg./g. body weight, 50% mortality.[61] Just before death the terminal plasma content of potassium in mg./100 ml. was in rabbits 58–85,[59] in dogs 89–149.[63-64] Death occurred at a much lower plasma level in dogs with severe myocardial infarction.[64] Oat hay may contain sufficient potassium nitrate to kill cattle, since a lethal dose, 25 g., might easily be contained in 5–6 lb. of hay.[65] The toxicity of potassium salts also depends on the age of the animal. Thus, 1 mg./g. body weight is not lethal for very young mice up to 3 days old but the mortality due to this dose thereafter increases with age up to 100% at 9 days, finally decreasing after 5–6 weeks of age to about 20% for mature mice. Somewhat similar behaviour is shown by other species.[62,66-68] Mice subjected to lethal radiation doses of *X*-rays show increased tolerance to potassium chloride followed by decreased tolerance, and a similar behaviour occurs during starvation.[69] A lethal dose of potassium chloride in mice may be counteracted by the simultaneous injection of 10–20 mg. of sodium chloride solution but not by calcium chloride or glucose.[60] The potassium tolerance of mice is greatly increased by injection of glutathione, which protects for at least 6 hr.[70,71] Prolonged administration of potassium chloride in the diet of rats causes the weight of the kidneys to increase, that of the heart to decrease and the glomerular zone of the adrenals to become hypertrophied.[72,73] The hearts of rabbits and mice injected with potassium chloride stopped in diastole.[74] Potassium autointoxication has been observed in rabbits owing to intravascular haemolysis of the red cells which released sufficient potassium to stop the heart.[75]

The lethal effect of potassium chloride to man depends more on the concentration of the solution and the rapidity of injection than on the absolute amount administered. Rapid injection does not allow time for the re-establishment of electrolyte equilibrium and a condition of shock results, the symtoms being tachycardia, fall of blood pressure and finally paralysis of the respiration and the heart.[76] Oral administration of potassium salts (equivalent to about 20 g. of potassium per person) results in a tetanic syndrome with paraesthesia and cramps of the hands and feet, followed by adynamia and muscular hypotonia for 24 hr.[77] Potassium intoxication may result from adrenocortical insufficiency[78] and administration of potassium salts may be dangerous in cases of renal failure.[79] Symptoms are produced more readily in subjects who have been on a low-potassium diet[80] and the typical symptoms appear to be due to a small but rapid increase of potassium inside the cells of the heart and kidneys.[81] Potassium autointoxication may occur in acute uraemia but the symptoms rapidly disappear after injection of isotonic sodium chloride.[82,83] As with animals, glutathione has a protective action against potassium over-dosage.[84] The use of potassium salts in therapy has recently been reviewed.[85] Favourable results have been obtained in the treatment of allergies such as hay fever, asthma and sinusitis by administration of potassium salts.[86-88]

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(v) Metabolism

There exist a number of recent reviews on the general metabolism of potassium in health,[1-5] on disturbances or abnormalities of metabolism[6-10] and on the disturbances of metabolism during disease or pathological states.[11-15]

Control of the concentration of potassium in the blood has been ascribed to various regions of the brain; thus such regulatory centres have been reported in the sinus caroticus,[16] in the optic thalamus[17] and in the corpus striatum, the last being said to control the concentration ratio of potassium and calcium.[18] There is now considerable evidence that the regulation of potassium metabolism is an important function of the adrenal cortex.[19] Cortin, ACTH, cortisone and deoxycorticosterone are all active in reducing the plasma concentration of potassium to subnormal levels.[20,21] All these agents appear to affect the rate of entry and exit of potassium into and out of muscle cells, ACTH and cortisone tending to reduce extracellular potassium,[22] while deoxycorticosterone inhibits the transport into the muscle cells to a greater degree so that the cells lose potassium.[23] Adrenalin administered intravenously also causes a marked increase in the concentration of potassium in the blood plasma. There is some evidence that this potassium is derived from the liver. The increase is only temporary, the excess potassium being rapidly taken up by the tissues.[24,25] Thus the intravenous injection into a cat of 0·5 ml. of a solution of 1;10,000 adrenalin causes a 65% increase in the serum potassium which returns to normal within 15 min.[26] It is estimated that each molecule of adrenalin may control about 10^5 potassium ions.[27] The intracellular:extracellular ratio of potassium appears to have some influence on the response of animals to adrenalin and also on the basal metabolic rate.[28] It is possible that one function of adrenalin is the maintenance of a constant concentration of potassium in the tissues.[29] While the ratio in milliequivalents of sodium to potassium ions in muscle has been found to be about 3 in normal rats falling to 1·9 after adrenalectomy, the ratios are smaller in the presence of glucose but the same difference is apparent.[30] It has also been shown conclusively that the injection of potassium salts stimulates the release of adrenalin by the adrenals.[31-36] An adequate supply of dietary potassium is essential for the replenishment of protein in starved animals.[37] Infection by a number of micro-organisms was associated with an increase in the plasma-potassium concentration in rabbits, and fatalities could be prevented by reducing the potassium concentration by means of cortin.[38]

Potassium appears to be intimately connected with carbohydrate metabolism.[39] Thus, injection of potassium chloride leads to a fall in the blood glucose content,[40] while the administration of glucose conversely leads to a fall in the serum potassium content.[41] Potassium reduces the oxygen uptake of many organs and tissues[42,43] and appears to play a part in the production of lactic acid by ram and bull spermatozoa.[44] Injection of potassium reduced the blood sugar level in artificially produced diabetes,[45] while the potassium level of serum is reduced through conversion to the intracellular phase by administration of insulin.[46] Acidosis interferes with this action of insulin.[47] Potassium is definitely concerned in glycogen synthesis by rat liver for if half the potassium is replaced by the equivalent amount of sodium ion the synthesis of glycogen is reduced. Potassium appears to be concerned principally in the phosphorylation of glucose by hexokinase.[48-50] High concentrations of potassium reduce the rate of glycogen synthesis as does the addition of deoxycorticosterone.[51-53] As the potassium concentration of the medium surrounding spleen tissue cultures was increased, growth was progressively inhibited while the amount of glycogen passed through a maximum.[54] Both ammonium ion and potassium ion have a direct stimulatory effect on glycolysis by rat tissue which is not antagonised by sodium ions and seems to be connected with phosphorylation reactions.[55] Aerobic respiration, however, is only slightly affected by reducing the concentration of either potassium or calcium, but is markedly inhibited if both ions are absent.[56,57] Potassium salts strongly increase the oxygen consumption and lactic acid production in brain and this effect is completely inhibited by malonate, azide or narcotics.[58-61] The respiration of rat liver mitochondria is enhanced by the presence of potassium, rubidium or cæsium but not by sodium or lithium, the effect being greatly increased by the addition of a heat-stable, acetone-soluble extract of microsomes.[62-64] Potassium has also been reported to be involved in the fatty acid metabolism.[65]

The concentration of potassium in human parotid saliva has been found to remain constant and independent of the secretory rate. This is in contradistinction to the behaviour of sodium.[66-69] The concentration ratio of sodium to potassium in the saliva varies during the day from 0·25 to 0·42 and is highest early in the morning. This variation may be due to a variation in the secretion of adrenocorticotropin since this hormone has been shown to control the ratio.[70-72] The concentration of potassium in tears is also independent of the rate of secretion.[73]

(vi) Sweat and temperature regulation

Sweating is an important method of excretion of potassium salts and between 3 and 100 mg. of potassium may be lost per day by this route.[74] The normal potassium content of sweat lies in the range 0·025–0·048% but may fall as low as 0·008% during profuse sweating.[75,76] The potassium concentration decreases with the rate of sweating[77] and also with progressive sweating, decreasing from an initial high value to a constant level in about 15 min.[78,79] The content was not affected by prehydration nor by repetition of the thermal stress or exercise.[80,81] Sweat collected after exposure to 100° F. contains more potassium than at 120° F.[82] There was no apparent correlation between either the sodium or the chloride concentration and the potassium concentration of sweat.[83] There was a slight rise in potassium content of sweat in cold weather. Significant differences were found in the potassium contents of sweat collected from different parts of the body, sweat collected in arm bags having, for instance, a higher content than total body sweat.[84,85]

(vii) Excretion

There are a number of recent reviews on the excretion of potassium in the urine.[86-91] The potassium content of urine normally ranges from 0·097 to 5·68, mean 2·38 g. per l., so that a total of 1·56 to 6·66, mean 3·48 g., may be excreted per 24 hr.[92] The rate of excretion of potassium remains constant after drinking water even though the urine production varies between 0 and 12·6 ml./min.[93,94] Beer, on the other hand, is not only a more powerful diuretic than water but it also decreases the output of potassium while increasing that of sodium.[95] Although the kidneys are able to conserve potassium to a limited degree, continued urinary loss together with restriction of potassium in the diet leads to a deficiency of the element. The urine produced under these conditions is more alkaline. Restriction of the sodium intake prevents this loss of potassium.[96] Breathing 5–7% carbon dioxide causes diuresis with no increase in the amount of potassium excreted.[97] A definite correlation has been established between sodium and potassium excretion and pH.[98] Thus the infusion of potassium chloride into a dog produces a decrease in plasma pH and bicarbonate concentration, while the infusion of sodium bicarbonate produces a decrease in the plasma concentration of potassium ion, followed by increased excretion.[99] The normal alkalosis produced by ingestion of sodium bicarbonate is prevented by the simultaneous ingestion of potassium salts.[100] Both potassium and bicarbonate ions depressed the hydrogen ion concentration of the urine.[101] The rate of excretion of potassium, as for sodium, depends on the activity and posture of the subject, quiet standing causing the rate of excretion to be depressed.[102] The intravenous injection of potassium chloride increases the flow of urine much more than does sodium chloride.[103] An increase of magnesium in the diet causes a decrease in the elimination of potassium in the faeces.[104] Exposure to extremes of both cold[105] and heat[106,107] appears to cause increased excretion of potassium in the urine in both animals and man.

Urine is formed by filtration in the glomeruli of the kidneys of a fluid of constant composition followed by subsequent reabsorption and possibly secretion of a portion of the dissolved electrolytes in another portion of the renal tubules.[108] Analysis of fluid from different parts of the tubules of rats indicates that potassium is actively reabsorbed by the proximal convoluted tubules[109] while there is evidence from a number of sources that potassium is also secreted by the distal tubules.[110-113] This tubular secretion acts as a mechanism to prevent the toxic accumulation of potassium in the body fluids. Both potassium and hydrogen ions appear to be excreted in exchange for sodium ions, the rate and relative division of the exchange being determined by the respective concentrations.[114,115] A diet rich in potassium produces an increase in excretion of 17-keto steroids and an inhibition of reabsorption of potassium, and it is thus possible that reabsorption is controlled by steroids.[116,117] It is also suggested that excretion of potassium may be controlled by the degree of tissue-cell saturation with this ion. Injected labelled potassium salts are very rapidly taken up by the kidneys and are later redistributed to other organs.[118] The rate of excretion in the urine is however much slower, only 11% being excreted in 48 hr.[119] Increase of the ureteral pressure causes a marked decrease in potassium excretion because of the reduced filtration rate.[120] The whole problem of electrolyte regulation in relation to the excretion of potassium has been extensively discussed.[121] The excretion of potassium is depressed by adrenalin and nor-adrenalin probably because of augmented tubular reabsorption, although the accompanying increase in total urine flow suggests that the hormones also interfere with the tubular reabsorption of water.[122,123] It is also suggested that nor-adrenalin may act by diminishing the tubular secretion of potassium.[124] The sodium: potassium ratio also rises and the action seems to be identical with that produced by the antidiuretic hormone.[125] In contrast, cortisone,[126] deoxycorticosterone[127] and adrenocorticotropin (ACTH)[128] all increase excretion of potassium because of inhibition of renal tubular absorption. There is some evidence for the production by the adrenal cortex of a specific salt-retaining hormone, not identical with cortisone.[129] Pituitrin and pitressin, but not pitocin, cause an increase in potassium excretion.[130,131] The hypophyseal growth hormone increased potassium excretion in rats[132] while vitamin E decreased excretion.[133]

There is a marked diurnal rhythm in the excretion of potassium which is linked to the simultaneously occurring rhythm in the acid and alkali excretion.[134,135] Although the normal cycle is 24 hr. some individuals appear to have a 12 hr. cycle. The rate of excretion of potassium is minimal at 2 a.m. and maximal at 10 a.m.[137] Seasonal and geographic variations may be superimposed on this nyctohemeral rhythm.[138] This excretory rhythm does not appear to depend on adrenal hormones.[139]

Ion exchange resins have come into therapeutic use for the control of the electrolyte balance of the body. Different types of resins are available and the ion predominantly excreted depends on the type and form of the resin. Thus a resin in the sodium form may exchange this sodium for potassium,[140] while another resin in the hydrogen or ammonium form has been found to absorb sodium, potassium and magnesium in the ratio of 11:5:1 respectively.[141] A procedure has been described for determining the exchange capacity and the optimum potassium content for clinical use.[142] Considerable quantities of potassium may be removed from the body by feeding the resins.[143,144] Most of this potassium comes from the cells and there may be a temporary increase in the blood concentration of potassium and an increase in excretion via the urine.[145] Simultaneous administration of ethylenediamine-tetracetic acid and a cation exchange resin resulted in a marked increase in the capacity of the resin for sodium and potassium.[146] The amount of potassium bound by a resin depends directly on the speed of transit through the gastro-intestinal tract, in contradistinction to the behaviour of sodium.[147,148] Rats after whole body *X*-irradiation lose potassium from bone and bone marrow with a resultant increase in the urinary and faecal excretion of potassium.[149] Rubidium behaves very like potassium in the body, the urinary excretion being 52% of that of potassium. Both elements may be excreted without entry into the major body compartments.[150]

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(viii) Physiological effects of potassium

(*a*) Action on the whole organism.

Following the intravenous injection of a 1% solution of potassium chloride there is a relative decrease in the lymphocytes and monocytes and an increase in neutrophils in man[1] while the red blood cell count is increased in most cases.[2] Potassium may markedly accelerate haemoglobin formation, particularly when the diet is low in iron.[3] Injection of potassium chloride in doses of 0·03–0·08 g. per kg. causes hyperglycaemia in fasting rabbits,[4,5] and may also cause a transient recovery in dogs in insulin coma provided this coma is not of the irreversible type.[6] Potassium has a marked hypertensive action, injection of 15 mg. per kg. in dogs causing a rise of about 50 mm. in arterial blood pressure,[7] while conversely restriction of the intake of potassium in the diet lowers the blood pressure.[8,9] Injection of potassium chloride also causes an increase in the blood calcium of dogs and counteracts the curariform paralysis produced by injection of magnesium salts.[10] The potassium ion appears to stimulate the growth of both normal and neoplastic tissues. Not all types of carcinoma, however, are stimulated to growth.[11,15] Potassium ions cause an increase in the absorption of glucose through the intestinal wall in dogs,[16] though absorption may be decreased in some parts of the intestine.[17] Potassium chloride appears to stimulate the secretion of gastric juice by dogs,[18] but the action of potassium iodide is very slight.[19] Potassium ions also depress the rate of respiration probably through direct action on the receptors of the carotoid sinus[20,21] and act as a synergist to thyroxine,[22,23] and to some convulent drugs such as pyramidone and codeine.[24] Injections of potassium salts produce characteristic skin reactions with persistent localised inflammation and pain.[25,26] Potassium and calcium ions appear to produce opposing and reversible effects on colour vision.[27] From time to time attempts are made to explain the biological effects of potassium in terms of its natural radioactivity, but experiments fail to prove this.[28-34]

(*b*) Effects on Muscle.

The potassium content of muscles appears to be related to function; thus white rabbit muscle, capable of rapidly contracting, contains 20–30% more potassium than red muscle, capable of only slow contraction[35,36] and after section of the nerves to the muscle the content decreases considerably.[37] Histochemical localisation of potassium in muscle fibres shows a general distribution throughout the fibre,[38] and a close association with glycogen deposits, noticeable where these are prominent, as in cases of infarction.[39] It is claimed that the major part of the potassium is localised in the anisotropic zones of the myofibrils, being retained there by electrostatic forces.[40] There is a high degree of correlation between muscle potassium and serum bicarbonate and intracellular sodium concentrations.[41] Injection of potassium chloride solutions results in a transitory rise in muscle potassium which returns to normal in about one hour.[42] The skeletal muscles of many species which are helpless at birth such as dog, cat, rabbit, etc. have a low potassium content at birth and an abnormally long chronaxia. After a few days, however, when movement becomes more rapid, the potassium content and the chronaxia approach the normal adult values. At between one and two months of age the muscles contain a higher potassium content than at any other time of life.[43-46] The changes in intracellular and extracellular potassium of muscle during growth and ageing have been followed histochemically in the rat. The potassium concentration of whole skeletal muscles decreases during growth and continues to fall during senescence although the concentration inside the muscle fibres undergoes no significant change.[47]

Dietary deficiency of potassium results in a fall in muscle potassium and an accompanying decrease in the intestinal mobility of rats.[48,49] The potassium content of muscles varies with exercise and training, falling slightly between 20 and 48 hr. after exercise and subsequently being greatly increased 3–4 days later.[50] During the progress of atrophy of a muscle following denervation there is a steady fall in the potassium content as compared with a normal muscle, selective permeability being rapidly lost and potassium being exchanged for sodium inside the cells.[51-53] The potassium content of muscle is increased by respiratory acidosis caused by breathing a high concentration of carbon dioxide for 2–3 weeks.[54] Occlusion of the circulation by tourniquets or other means causes a loss of intracellular potassium, replacement by sodium and the resultant impairment of muscle function.[55-57] The muscle potassium content may be reduced in some pathological muscle states but not in others.[58-60] In some degenerative muscular diseases serum potassium is reduced,[61] but even where this is unchanged there is usually a marked decrease in exchangeable potassium.[62] It has been suggested that the cause of death in a case of delirium tremens was an abnormally high serum potassium concentration, the potassium being derived from muscles maintained in severe, continuous activity.[63] A similar rise in serum potassium accompanied by muscular pain and weakness has been observed as a result of excessive exercise of the forearms.[64] A 15% reduction in muscle potassium may be sufficient to explain the 'kangaroo' posture of biotin-deficient rats.[65] Muscles can become paralysed when the surrounding solution contains too high a concentration of potassium,[66,67] and present knowledge of the role of potassium in many muscular diseases has been reviewed.[68,69] In congenital myotonia the muscles are five times as sensitive to potassium as normal muscle.[70] In familial paralysis the serum potassium concentration is greatly reduced, but the immediate cause of attacks is the lowering of intracellular muscle potassium, since attacks are not caused by reduction of blood serum potassium after injection of adrenal cortex extracts.[71,72] Potassium excretion is actually decreased during attacks. There is some evidence that the potassium content of the muscles is reduced as a result of increased intermediate carbohydrate metabolism in the liver.[73-75]

Calcium and potassium salts appear to have opposing effects on isolated intestine and uterus, potassium having a depressing effect on low and a stimulating effect on high concentrations, while calcium behaves in exactly the opposite manner.[76,77] After injection the two salts similarly have opposing actions on the contractions of the frog stomach, potassium chloride causing cessation of motility while calcium chloride causes the development of slow wave-like contractions.[78] These effects have been correlated with the known effects of the two ions on membrane permeability and potentials, irritability and chronaxia.[79] Introduction of potassium chloride into the central nervous system increases the chronaxia of the skeletal muscles while calcium chloride has the opposite effect.[80] Isolated rabbit intestine is paralysed by solutions of magnesium chloride but not by mixtures of potassium and magnesium chloride, suggesting a similar opposition between the effects of these two ions.[81] Potassium ions oppose the action of adrenalin on the isolated frog stomach,[82] while adrenalin abolishes the paralysis caused by potassium ions on the rat phrenic-diaphragm preparation.[83] Injection of adrenalin causes an initial decrease followed by an increase in the rate of loss of potassium by muscle.[84,85]

Potassium ions are released from muscle during stimulation.[86-89] Potassium salts appear to have a direct action on the muscle fibre itself and not exclusively on the neuro-muscular transmission.[90,91] Thus the ion causes contraction even during deep narcosis,[92] while *in vivo* injection of potassium salts causes contraction in muscles which have been denervated 6–14 days previously.[93] There is also considerable evidence that potassium is concerned in the neuro-muscular transmission, perhaps by stimulation of release of acetylcholine.[94-98] The amount of potassium released during contraction was found to be related to the number of stimuli applied to the muscle and not to the total tension developed.[99] The release of potassium ions during contraction is accompanied by a decrease in volume of the muscle which agrees with the volume decrease associated with the ionisation of the same amount of potassium.[100] Attempts have been made to correlate penetration of potassium ions into the muscle fibres with changes in twitch tension and recovery,[101,102] and with the heat production.[103] A threefold action has been suggested for potassium: first, an action due to the difference in concentration of ions on both sides of the muscle membrane; second, a direct action on the membrane itself antagonised by calcium ions; third, an action on the muscle colloid itself.[104] The importance of calcium is shown by the fact that pretreatment with citrate or oxalate (which would precipitate calcium ions) abolishes response of muscle to potassium.[105,106] Both calcium and potassium ions seem to be required for the polymerisation of actin[107] while myosin threads[108] and surface-spread actomyosin fibres[109] contract and elongate as the concentration of the surrounding potassium chloride changes. The influence of potassium and calcium ions on the electrophoretic behaviour of myosin has also been studied.[110] Adenosine triphosphate is concerned in the contraction of muscle fibrils under the influence of potassium and it has been suggested that this substance removes or inactivates some compound which inhibits the dissociation of bound cations.[111] Some thermodynamic studies have been carried out on the contraction of tendons treated with potassium chloride.[112,113] The reversible dismutation of adenosine triphosphate by myokinase is strongly inhibited by potassium, sodium, magnesium or calcium chlorides when these have an ionic strength greater than 0·6.[114]

There have been several attempts to demonstrate that not all the potassium in muscle is freely diffusible but that a considerable proportion is 'bound' in some way, a fraction of this 'bound' potassium being released during each contraction of the muscle and being returned during relaxation,[115-120] but this has proved very difficult to confirm.[121-124] When muscle is immersed in a solution containing 0·010% of potassium ion, potassium diffuses from the muscle to the solution but if the concentration of the solution exceeds this value potassium enters the muscle.[125,126] The potassium content of muscle is also changed after damage or injury. Anoxia leads primarily to an increase in the rate of outflow of potassium whereas exposure of the muscle to cold results mainly in a decrease in the rate of influx of potassium.[127,128] Denervation of muscles also causes a substantial increase in the rate of loss of potassium.[129,130] The rate of loss is increased by histamine,[131] strophanthin or 2,4-dinitrophenol.[132,133] The electric excitability of frog gastrocnemius muscle is not lost until 70% of the potassium has diffused out.[134] Studies with the radioactive isotope ^{42}K have shown that the extracellular space of the rat *extensor digitorum longus* muscle is 0·10–0·15 of the total volume and that the potassium in this space exchanges with a half time of 5–7 min. as compared with a half time of 1·5 hr. for the intracellular potassium.[135] Although the rate of exchange is about the same in normal and dystrophic muscle,[136] the total potassium exchanged in a given period in the whole body is reduced in cases of muscle dystrophy.[136] Observations of the exchange of potassium and water by stretched and unstretched muscle immersed in solutions of different concentration indicate that muscle cannot be regarded as a simple osmotic sac.[137] The potassium flux in frog muscle in 2·5 mM. potassium chloride is 4·5 μM./cm.^{2}/sec.$^{-1}$, the flux doubling in 5 mM. solution.[138] The efflux of potassium from muscle can be reduced by increasing the calcium content of the surrounding solution and the effect of calcium in turn abolished by once more increasing the potassium concentration of the solution.[139,140] Some evidence has been adduced that potassium does not penetrate through the cell walls but into the extracellular space.[141,142] The potassium content of muscle depends on the pH of the surrounding solution[143] and potassium ions can exchange with hydrogen ions. The velocity constant of ion exchange at 25°C. calculated as a second order reaction is 1·68 × 10^{-3}.[144] It has been shown by several different techniques that the formation of glycogen from glucose and the uptake of potassium by muscle are coupled in some ways.[145-147] It has also been well established that there is a reciprocal relationship between the content and movement of sodium and potassium ions in muscle.[42,148-150] Early attempts were made to explain the ion distribution by means of a Donnan equilibrium between potassium and chloride ions separated by the muscle membrane,[151,152] but it is now generally agreed that the distribution must be due to active transport, *i.e.*, that the muscle membrane is freely permeable to ions, that the internal concentration of potassium is maintained by means of an electrochemical gradient and that sodium which can freely enter the cell is actively transported outwards by a sodium extrusion mechanism (the so-called 'sodium pump').[153] (See also Volume II, Supplement II, page 1430).

Potassium leaves the interior of the cell and is replaced by sodium during contraction while during relaxation sodium is actively extruded and potassium re-enters the cell.[154] If the outward movement of sodium is stopped, there is no accumulation of potassium, which suggests that the important factor is extrusion of the sodium ion.[155]

Potassium is able to induce contractions in muscle which has been fatigued through being deprived of oxygen.[156] Potassium ions in solution up to a a concentration of 0·035–0·045% increase the oxygen consumption of muscle because of the breakdown of phosphocreatine, but at concentrations above 0·060% phosphocreatine is re-synthesised.[157] The element appears to aid the transfer of phosphate from 3-phosphoglycerate to creatine.[158] It is claimed that a relaxing factor has been isolated from muscle which induces relaxation, the action being inhibited by potassium ions.[159]

From known relative permeability coefficients of potassium, sodium and chloride ions the muscle membrane potential has been calculated and found to agree well with measured values.[160] The breakdown of the membrane potential is accompanied by liberation of potassium ions following destruction of the membrane.[161] The degree of depolarisation of frog *sartorius* muscle is linearly related to the logarithm of the potassium ion concentration in the external medium. The rate of depolarisation by 0·1 M. potassium chloride is very rapid at the fibre surface and from a study of the rate of depolarisation of bulk muscle the diffusion coefficient of potassium into the muscle, which is the limiting factor, is 10^{-4}cm.^{2}/min.[162] A potential of 80–120 V. appears to be necessary to recharge muscle membrane depolarised by potassium chloride.[163] The injury potential of frog muscle is not completely abolished by removal of 99% of the potassium ions through soaking in water.[164] Although potassium and magnesium ions have similar effects on muscle impedance measured at high frequencies, they have much the same effects on polarisation.[165]

Rats maintained on a potassium deficient diet for long periods develop an abnormal carbohydrate metabolism in the muscles whose pH is also lowered.[166] In such rats acetyl-β-methylcholine stimulates intestinal motility although it is without effect on normal rats.[167] Veratrine and sodium thiocyanate augment the action of potassium ions on guinea pig ileum.[168] Potassium ions are strongly antagonistic to curare and synthetic curarising agents,[169,170] but curare does not liberate potassium ions from muscle and its activity thus does not depend on potassium.[171] Muscle relaxing agents such as succinylbischoline or decamethonium do cause the liberation of potassium from muscle and this liberation is neutralised by curare.[172,173] The paralysing action of strophanthin is also accompanied by a release of potassium from muscle.[174] Many agents such as caffeine, theobromine and theophylline increase the sensitivity of muscle preparations to potassium ions.[175] With some drugs such as veratrine the sensitisation is an action on the muscle fibre itself, while other drugs such as guanidine, aminopyridine or tetraethylammonium salts appear to sensitise by acting on the myoneural synapses.[176] Indole and many of its derivatives enhance the action of potassium on striated muscle but inhibit the action on smooth muscle.[177,178] Although morphine potentiates the effect of potassium on frog muscle,[179] many other local anaesthetics desensitise the response.[180,181] Vitamin *A* and calcium pantothenate also decrease the sensitivity to potassium[182] while potassium ions cause sensitisation of muscle in different degrees to many drugs, e.g. neostigmine, pilocarpine, eserine, etc.[183]

(*c*) Effects on Heart and Vascular System.

Although differences are frequently found in the potassium contents of the right and left ventricles, these differences can be attributed to differences in water, fat and connective tissue contents.[184] Rubidium behaves very like potassium in its action on the heart whereas caesium is different.[185] Calcium and potassium have opposing actions on the mammalian heart.[186] Thus calcium salts neutralise the toxic effects of potassium on frog heart.[187] Magnesium ions intensify the action of calcium but cannot replace it.[188] The combined effects of potassium and calcium in the contractibility and excitability of the mammalian heart show some differences from the action on the frog heart.[189] It has been deduced from the temperature coefficient of the heart beat that potassium is the dominant ion for automaticity and calcium for amplitude.[190,191] An increase in the potassium concentration of the perfusing fluid causes diastolic arrest of the isolated heart, while increase in calcium causes the heart to stop in systole.[192,193] The well-known inhibitory action on the heart of vagus nerve stimulation may be due to the liberation of free potassium ions inside the muscle cells.[194] This action of the vagus is diminished by increasing the ratio of potassium to calcium ions in the perfusing fluid and intensified by reducing the ratio.[195] In some circumstances the actions of the vagus and sympathetic nerves may actually be reversed by altering the concentrations of ions, the vagus being made to stimulate and the sympathetic nerve to inhibit.[196] Potassium ions stimulate the cardiac accelerator and inhibitor centres of the brain.[197,198] Increase of temperature antagonises the action of potassium on the frog heart.[199] The actual effect of potassium ions depends on the previous history of the heart and may be reversed after certain treatments.[200] Potassium ions act on the heart in the opposite manner to acetylcholine and from the comparison of the actions of the two substances it is concluded that potassium has a negligible influence on the transmission of vagal nerve impulses to the auricle but that acetylcholine is the effective agent.[201-203] There is some evidence that acetylcholine is connected with the transfer of sodium and potassium ions through the walls of the myocardial fibres.[204,205] The action of adrenalin on the heart depends on the presence of potassium and calcium.[206,207]

The effects of potassium on the electrocardiogram have been described.[208] Electrocardiographic abnormalities appear to be correlated with the intracellular potassium content rather than with serum potassium since considerable changes in the serum potassium may occur without effect on the electrocardiogram.[209,210] The most characteristic sign of raised blood potassium, however, is an increase in the amplitude of the T wave,[211,212] which during fatal potassium intoxication becomes tent-shaped.[215,216] Direct application of potassium chloride solution to the *sinus venosus* of the exposed frog heart caused definite signs of de-synchronisation between the two halves of the heart.[217] An increase in the potassium concentration of the surrounding solution up to 0·020% increased the excitation conduction of frog heart strips but greater increases reduced conduction until blocking occurred eventually.[218] There is a continual exchange between cellular and extracellular potassium in the isolated frog heart.[219] During fatigue rat heart strip preparations were observed to lose 13·7 mM./kg. of potassium ion and to gain 23·9 mM./kg. of sodium ion.[220] The average transfer rate between the interstitial and intracellular pools in the left ventricle of the dog heart is approximately double that between plasma and interstitial pool.[221] Potassium promotes the synthesis of creatine phosphate in the heart[222] and a significant decrease in dipotassium phosphocreatine was found in cases of congestive heart failure.[223]

Injections of potassium chloride tend to suppress auricular fibrillation[224] but the effect is much weaker than that of quinidine.[225] Slow intravenous injection of potassium salts brings about intraventricular block and diastolic arrest. It is unlikely that toxic concentrations will be attained in man by oral ingestion.[226] The subject of cardiac arrest by potassium has been reviewed,[227] and electrocardiograms described.[228] In the rabbit injection of potassium chloride produces widespread block in all parts of the heart, but if the injection is rapid ventricular fibrillation ensues.[229] In the isolated heart such fibrillation is induced by a rapid elevation of concentration of calcium ions to a critical concentration which is dependent on the actual prevailing potassium concentration.[230] In cases of congestive heart failure there is a marked loss of cardiac potassium owing mainly to overwork.[231]

The action of caffeine on the heart consists of a sensitisation to the effect of potassium.[232] Potassium decreases the action of aconitine on the ventricle.[233] Chloral hydrate and potassium have similar toxicological properties,[234] while strophanthin markedly increases the action of potassium chloride on the heart.[235] Digitoxin or digoxin causes an increase in plasma potassium in dogs sufficiently high to produce arrhythmia.[236] Ouabain increases the paralysing action of potassium salts on the frog heart[237] but camphor derivatives have an antagonistic action on potassium intoxication.[238]

A method for the determination of cardiac output using ^{42}K has been described and claimed to have many advantages over other methods.[239] It has been claimed that the biological effect of potassium on the heart is due to the presence of the natural radioactive isotope and that uranium ions or radon may be substituted for potassium.[240-242] It has been shown, however, that uranium cannot replace potassium and that the action of the radioactive elements is quite different.[243-246]

By direct observation on frogs it was found that potassium ions are without effect on the blood vessels of the lung, cause constriction of the intestinal vessels and dilation of those of the kidney and adrenals.[247] Potassium causes constriction of the coronary blood vessels of warm-blooded animals[248] and in general appears to be vasoconstrictive in contrast to calcium.[249,250] Repeated injection of solutions of potassium chloride into rabbits induced the formation of a thin, loose, flattened vascular membrane.[251] Injection of 1–5 mg./kg. of potassium chloride into dogs causes a marked if transient rise in blood pressure which appears to be due partly to a release of choline and an adrenalin counteraction and partly to direct entry of the cation into the smooth muscle fibre.[252-255]

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(*d*) Effects on Brain and Nerve Cells.

The role of potassium in the activity of nerve cells has recently been reviewed.[1,2] Wide variations are found in the potassium content of fresh nerve tissue of small mammals; thus in cats, dogs and rabbits the range[3] is from 0·076 to 0·360%. Starvation for only two days causes potassium to be lost from nerve cells.[4] Asphyxiation also causes increased losses[5] while polarisation by the application of a steady potential kills frog nerves and results in migration of all the contained potassium.[6] Extraction of potassium compounds from brain and nervous tissue with lipoid solvents under various conditions suggests that the element is present in more than one form, one of which is soluble in water-free alcohol or ether.[7,8] There is a steady exchange between the potassium of adult rat brain and that of the blood plasma and measurements of the efflux and influx indicate that all the brain potassium is freely exchangeable.[9] Similar measurements with ^{42}K, however, suggest that this is true for young rats but not for adults in which 20 mg.K/kg. wet brain tissue fails to exchange with the plasma potassium.[10] The grey matter of rabbit brain contains slightly more potassium than the white matter.[11] Autoradiographic methods show that the distribution in rat brain of ^{42}K after intraperitoneal injection is fairly homogenous, slightly higher concentrations being found in the cerebral and cerebellar cortex, basal ganglia and in the roof of the fourth ventricle.[12] The radioactive isotope, ^{42}K, has been found useful for the location of cerebral tumours since it tends to accumulate in tumour tissue.[13] Characteristic changes in the electro-encephalogram were caused by increasing the potassium content of the fluid perfusing the cerebral ventricle of cats.[14]

Potassium salts appear to have a stimulating action on isolated nerves while calcium ions have a depressing effect.[15,16] It is possible that a definite ratio between the concentrations of the two ions is necessary for correct functioning of all nerves.[17-19] An increase in the concentration of potassium can counteract the effects of calcium deficiency in the nerve.[20] Cochlear microphonic and action potentials were reduced by increasing the concentration of potassium chloride in the fluid perfusing the guinea pig cochlea.[21] Potassium ions acting on the retina of the excised frog eye caused characteristic changes in the electro-retinogram.[22] Administration of potassium hydrogen phosphate to dogs stimulates the sympathetic and inhibits the parasympathetic centres, thus depressing gastric secretions and decreasing motility of the stomach.[23]

The general behaviour of sodium and potassium ions in nerve conduction is now well-known, although an exact explanation of their role is not yet possible. (See also Volume II, Supplement II, page 1431). In resting nerve there is inside the axon a high concentration of potassium and a low concentration of sodium ions, the opposite situation existing outside the axon. As a result a well-defined membrane potential exists between the inside and the outside of the nerve fibre. Passage of an impulse along the nerve causes sodium ions to enter the axon and potassium ions to leave until the membrane potential is reduced to zero and even reversed. In the recovery process which follows, sodium ions are actively transported out of the axon by the so-called 'sodium pump' mechanism and potassium ions enter to restore the resting state.[24] Application of solutions of potassium chloride stronger than physiological (0·9%) to the myelin sheath of a nerve prolongs the transmission time across the treated segment[25] and blocks conduction by the nerve owing to depolarisation.[26-28] The inexcitability of nerves after asphyxia in nitrogen has been shown to be due to release of potassium by the nerve fibres, and its accumulation in the interfibre spaces.[29] The energetics of the sodium–potassium transfer have been calculated.[30] The temperature at which conduction block occurs and also that at which the membrane potential is at a maximum appear to depend on the concentration ratio of potassium to calcium ions.[31] The rate of movement of potassium in rabbit nerve is decreased 4–5 fold by reducing the temperature from 18°C. to 0°C., while the rate of entry is diminished more than the rate of efflux so that the net result is a loss of potassium from the axon.[32] The sodium and potassium concentrations of the middle third of isolated frog nerve immersed in Ringer solution did not change significantly, for, although potassium was released all along the length of the nerve, the loss was replenished by diffusion into the middle from the end sections.[33] Potassium exchange from the superior cervical ganglia of rats, rabbits, cats and dogs incubated in saline containing ^{42}K had reached a steady state after four hours, but the exchange was only to a limited degree a first order reaction.[34] The rate of exchange was unaffected by removal of the axons.[35] The effects of various treatments (anoxia, cocaine, veratrine, glucose, etc.,) on the transport of sodium and potassium ions in frog sciatic nerve have been studied. The bioelectric potentials calculated on the assumption that the potential is due primarily to potassium ion migrations are consistently higher than the measured potentials.[36] The diffusion and exchange coefficients of the core of the frog sciatic nerve are estimated to be 1/300 of those in free aqueous diffusion.[37] There is a striking difference between the rates of diffusion of potassium into nerves with and without intact epineuria.[38] The average outward movement of potassium from whole nerves into normal Ringer solution has been measured as $1{\cdot}6 \times 10^{-5}$ of the internal potassium per impulse or $2{\cdot}7 - 3{\cdot}6 \times 10^{-12}$ mole per cm.^{2} per impulse. The rate of loss is roughly proportional to the stimulation rate.[39] The lowering of the stimulation threshold after treatment with barium salts has been ascribed to a decrease in the permeability for potassium.[40]

An increase in the potassium concentration of the solution surrounding an isolated nerve causes a decrease in the amplitude of the spike potential and in the after-potential, while recovery is delayed.[41,42] The amphibian nerve may be depleted of 50% of its contained potassium without affecting the amplitude of the action potentials, although the time course of depolarisation by externally applied potassium is lower.[43] The depolarisation of nerves by excess potassium ions may be inhibited by increasing the sodium ion concentration.[44] The different effects of temperature on the depolarisation of nerves by ions suggests that potassium and rubidium act by a different mechanism from that for ammonium or lithium ions.[45] Potassium ions increase the anelectrotonic potentials of frog spinal root nerves, while rubidium ions increase the nerve reaction.[46] The possible importance of the internal potassium concentration to the functioning of nerve and in particular to the maintenance of the resting potential has been critically examined, and it is pointed out that the presence of a high internal concentration of potassium is not alone a sufficient reason for ascribing great importance to this ion when there are other constituents present.[47] A mechanical model of a motor nerve could in fact be produced without the use of potassium salts.[48] A comparative study with nerves of different species of animals indicates that it is the fibre membrane which maintains the gradient of potassium concentration between the exterior and the interior and that the amount of myelin is unimportant for this.[49] Leakage of action current through the myelin sheath is increased by immersing the nerve in 4·5% potassium chloride solution.[50] Potassium behaves like a narcotic in its effect on the electrical rectification of nerves.[51]

Acetylcholine, liberated when a nerve is stimulated, antagonises the depressant action of potassium ions on the nerve.[52] Potassium ions are found to act as an inhibitor of cholinesterase so that the hyperirritability of motor nerve may be due to a delayed destruction of acetylcholine liberated at the endings.[53] The prolongation of the refractory period of frog sciatic nerve by potassium ions has been ascribed to their ability to liberate acetylcholine.[54] A lack of glucose or of potassium in the perfusing fluid causes a decrease in

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sensitivity of the superior cervical ganglia of the cat to acetylcholine.[55] The influence of potassium ions on the sensitivity to acetylcholine varies from organ to organ.[56] High concentrations of potassium ions accelerate the synthesis of acetylcholine by rat brain[57] and by normal superior cervical ganglia but not by axotomised ganglia.[58] There is some evidence that acetylcholine acts at motor end plates by raising the permeability to ions other than sodium, such as potassium.[59]

The highest concentration of potassium and also the highest respiration rate occur in the cerebellar cortex of the brain.[60] The oxygen uptake of rat cerebral cortical tissue is increased by the addition of potassium chloride, but this effect is abolished by participants in the metabolic tricarboxylic cycle.[61] Electrical excitation of brain produces a rise in the potassium content of the blood.[62] The influx rate of potassium from blood to the brain of adult rats was found to be 2·89 meq./kg./hr., the outflux being 3·64 meq./kg./hr. so that the influx/outflux ratio was 0·80, indicating that about 20 meq./kg. of potassium in the brain was not exchangeable with that in the blood.[10]

Potassium salts synergise the action of cocaine and many anaesthetics of the cocaine type.[63–65] Many narcotics produce changes in the distribution of potassium in the brain and central nervous system.[66]

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(*e*) Permeability and Active Transport.

The exchanges of potassium between the various organs of the body have been recently reviewed.[1] Exchange of potassium between organs and the blood plasma can now be easily followed by using a radioactive isotope of potassium. Exchange tends to cease after one or two days when only half the total potassium of the cells has been exchanged and thereafter there is no further change.[2] Cortisone, deoxycortisone and other hormones of the adrenal cortex have a marked influence on the penetration of potassium into cells, the effect being attributed to a specific action on the permeability of the cell membrane.[3-6]

Anomalies observed in the rate of loss of potassium from human erythrocytes have been interpreted as indicating that there are at least two types of cell.[7] Periodic variations have been observed in the potassium content of erythrocytes, maxima or minima occurring at about midnight and at 3–4 p.m.[8] It has been suggested that the potassium content of erythrocytes varies to maintain osmotic equality.[9] Hæmolysis studies indicate that potassium is not freely ionised within the red cell, but is possibly combined with the cell pro-

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teins.[10] On haemolysis potassium ions are liberated before hæmoglobin.[11] Exposure of red cells to ultrasonic vibrations similarly increases the potassium but not the haemoglobin content of the serum.[12] Melittin, a constituent of bee venom, also increases permeability of the red cell membrane to potassium and subsequently to haemoglobin.[13] Metallic poisons such as the chlorides of lead, mercury or gold[14] and also exposure to X-rays[15] increase the rate of loss of potassium from red blood cells. The cornea of the rabbit, cow and cat eye is more permeable to potassium than to sodium.[16-18] The rate of exchange of potassium ions between the amniotic fluid and the maternal system has been measured and found to be 0·0041 mole/hr.[19]

Active transport of potassium into cells is intimately bound up with the transport of sodium and hydrogen atoms.[20,21] (see also Volume II, Supplement II, page 1432). Although the dialysis of hæmoglobin against Ringer solution results in the accumulation of potassium and a corresponding depletion of sodium in the hæmoglobin compartments,[22] evidence has established that the ion distribution in the red blood cells is maintained by means of active transport, aided perhaps by the Donnan equilibrium.[23] Red cells take up potassium from hypertonic solutions of potassium chloride, but very little is taken up from serum with increased potassium content.[24] Storage of whole blood at lower temperatures results in a leakage of potassium from the cells to the serum owing probably to reduced enzyme activity.[25] The concentration distribution is restored by incubation at 37 °C. for some hours in the presence of glucose.[26,27] The normal cation distribution exists when active transfer exceeds passive diffusion and this state obtains in the pH range 7·3 – 8·0 at 37°C. with adequate glucose utilisation, 150–220 mg./l. red cells/hr.[28,29] Oxygen also appears to be necessary for the maintenance of the cation distribution.[30] Accumulation of potassium by the cells is linked with the transport of sodium, the rate of excretion of sodium being twice the rate of accumulation of potassium.[31] Evidence from the rates of exchange suggests that a single mechanism brings about active sodium expulsion, the accumulation of potassium being a passive process.[32] No evidence has been found linking cholinesterase activity with potassium accumulation in the red cell.[33] The distribution of sodium and potassium in kidney cortex cells cannot be explained by the Donnan effect [34] Rubidium and to a lesser degree cæsium may be substituted for potassium in active uptake by frog skin.[35]

Rabbit red cells treated with butyl alcohol lost potassium and gained sodium at the same rate.[36] Only about 2% of the red cell potassium exchanges with the plasma potassium during the lifetime of the cell in rabbits.[37] The rate of exchange is much higher in rats, about 5% of the intracellular content per hr. which is about 3·5 times the rate for human erythrocytes.[38] When red cells labelled with ^{42}K are injected into the blood stream the mean loss of potassium per hr. is 2·1% during the first day.[39] In dog red cells 94% of the intracellular potassium exchanged in 93 hr. The rate of influx depends on the external potassium concentration in the case of the dog red cell (unlike the human red cell which is independent of the plasma concentration[40]) and can be expressed by the equation:

$$\text{Influx (meq./l.cells/hr.)} = 0{\cdot}028\ [\mathrm{K}]_{\mathrm{amb}} - 0{\cdot}003$$

where $[\mathrm{K}]_{\mathrm{amb}}$ is the external potassium concentration.[41] The apparent activation energy under physiological conditions is 14,100 g.-cal./mole for dog red cells[41] and 12,300 ± 1300 g.-cal./mole for human cells.[42] The energy of exchange of sodium by potassium in human connective tissue is −1250 g.-cal./mole at 37°C.[43] The radioactive rubidium isotope ^{86}Rb is a very good tracer for potassium for erythrocyte studies since the mean exchange rate of potassium between red cells and plasma is the same measured with ^{42}K or ^{86}Rb as the tracer.[44] Unfortunately, the kinetics of exchange of potassium in the blood circulation fit a passive exchange mechanism but do not exclude an active transport.[45] When glycolysis is inhibited by sodium iodoacetate there is a greater net outward flow of potassium ions than of sodium ions into the cell.[46] There is active transport of sodium into frog skin. Potassium is normally excluded but if the skin potential falls below 30–49 mV. potassium is taken up.[47] The mean potassium flux through rat diaphragm has been measured as 21×10^{-12} equiv./cm.^{2}/sec.[48] Potassium uptake by kidney cortex tissue is correlated with aerobic oxidation and with oxidative phosphorylation.[49] The intracellular potassium of kidney cortex exchanges uniformly at 37°C. with rate constants of 0·206 and 0·145 min.$^{-1}$ aerobically and anaerobically respectively. Equations have been derived for the steady state uptake under the two states.[50] The turnover rate is 15%/min.[51] Active transport of potassium also occurs in kidney mitochondria, dependent on aerobic metabolism and with a turnover rate too fast to measure.[49,52] The turnover rate per minute of potassium in guinea pig brain slices is 3·5–4·0%, that of the retina 7–10%.[53] By studying the competition between alkali metal ions for entrance into red blood cells it has been found that sodium and potassium are transported by different systems.[54]

Various theories have been advanced to account for the selective transport of cations across cell membranes,[55,56] and a number of metabolic phosphorus intermediates have been proposed as carriers, but none seems entirely satisfactory.[57-60] Rat red cells utilise less than 0·5 mM. of glucose per mM. of potassium entering the cell, the human erythrocyte utilising nearly 1 mM.[38] Under aerobic conditions only about 6% of the available metabolic energy is required to maintain the potassium distribution in human red cells, but anaerobically between 190 and 2500% would be required.[61,62] Potassium accumulation by kidney and by red cells has been shown to be decreased by such metabolic inhibitors as cyanide,[63] cysteine,[64] arsenate,[65] fluoride,[66] *p*-chloromercuribenzoic acid[67] and strophanthidin.[68] Decouplers of oxidative phosphorylation also hinder potassium accumulation[69-72] and there is some evidence that adenosine triphosphate is intimately concerned in the process.[65] Many cells including erythrocytes suffer increased losses of potassium when treated with cholinesterase inhibitors and attempts have been made to connect potassium uptake with cholinesterase activity, but the evidence is not conclusive and there seems no clear relation between these two activities.[73-77] Nor can a definite connection be established between potassium uptake and carbonic anhydrase activity.[69,78] It has been claimed that *l*-glutamate is an essential substance for the transport of potassium in brain and retina[79] but this has been disputed.[80] The theory has also been put forward that the mitochondria are the organs which actually accumulate and secrete ions in cells.[81]

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6. ENZYMES

The role of mineral elements including potassium in enzyme systems, particularly those of plants, has recently been reviewed. In general potassium is regarded as an integrating activator, *i.e.*, one essential for enzyme activity but not strongly attached to the protein.[1] Studies of the dissociation of the methaemoglobin-azide compound show not only the ionic strength of the solution to be important but also the nature of the salt; thus the dissociation constant is 2·5 times as great in potassium iodide solution as in sodium chloride at the same ionic strength.[2] Misleading results may be obtained if sufficient care is not taken over experimental details; thus, potassium ions appeared to stimulate or to have no action on a cell-free bacterial apyrase depending on the order in which the components of the system were added to the Warburg flask.[3] Potassium ions have been shown to be essential for the correct functioning of the enzyme pyruvic phosphoferase.[4,5] Magnesium also appears to be needed and potassium can be replaced by rubidium or ammonium ions but not by sodium, lithium or calcium.[6,7] The Michaelis constant for potassium is 0·0114M. and kinetic analysis indicates that potassium, phosphopyruvate and the enzyme combine to form an active ternary complex,[7] though this has been denied.[8] This enzyme has been found to be widely distributed in mammals and in many marine species, the Michaelis constant varying somewhat from species to species.[9] Fructokinase also appears to be activated by magnesium and by low concentrations of potassium, high concentrations causing inhibition.[10] A ternary complex may also be formed in this case. Potassium ions strongly activate sucrase,[11] β-glucosidase,[11] catalase,[11] tryptophanase,[12] glutathione synthetase,[13] pantothenate synthetase,[14] the acetate-activating enzyme[15] and cytochrome oxidase.[16,17] There is weak inactivation of deoxyribo-

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nuclease[18] but inhibition has been reported on urease[19] and on succinic dehydrogenase,[20] the anion apparently playing an important role in these last two cases.

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CHAPTER 4

RUBIDIUM

SECTION LXII

THE OCCURRENCE OF RUBIDIUM

By P. C. L. THORNE AND K. W. ALLEN

Of the 0·03% of rubidium present in the earth's crust, 0·0075% is ^{87}Rb which has yielded 0·00025% of radiogenic strontium. Much of the strontium in pegmatites is of radioactive origin, and hence the age of the rocks can be calculated. Amazonites and pollucite contain from 0·1 to 1·5% of rubidium and less than 0·004% of strontium, while lepidolite averages 1·5% of rubidium and less than 0·01% of strontium.[1] An attempt has been made to deduce the age of limestones by the same method,[2] and the age of pegmatites from South-eastern Manitoba has been deduced as 2400×10^6 years, assuming a half-life of $5{\cdot}9 \times 10^{10}$ years for rubidium.[3] The ages of two phlogopites from South India have been estimated similarly as 1490×10^9 and 1630×10^9 years.[4] In a study of South African rocks[5] it has been found that the ratio Rb_2O/Tl_2O is remarkably constant for an area, lepidolites being richest in both elements with 1·5% Rb_2O.

In the U.S.S.R. rubidium (and cæsium) are reported in orthoclase and microcline[6] and in other minerals.[7,8] Lepidolites are reported with up to 0·85% Rb_2O, and this element is constantly found in spodumene from the Altyn-Tau deposits.[9] The colour of green amazonite was formerly[10] attributed to the rubidium content, but it now appears[11] to depend more on the presence of iron and manganese. In Southern Scotland rocks of the plutonic complex are reported to contain 50–380 p.p.m. Rb.[12] A comparison of rocks from Scotland and from North America has been made by spectrographic methods which gave, inter alia, concentrations of rubidium (and cæsium).[13] Rubidium contents of minerals in Arizona have been reported.[14]

Samples of water from oceans contain[15] $1{\cdot}1 - 2{\cdot}2 \times 10^{-5}$% Rb, while the Caspian Sea has only 3×10^{-6}% and Lake Inder $5{\cdot}7 \times 10^{-4}$%, but Japanese coastal waters contain[16] $2{\cdot}5 - 4{\cdot}0 \times 10^{-5}$%. The rubidium content of plants (11·2 – 31·2 p.p.m.)[17,18] and of soils[19] has been determined. The content of green coffee grains[20] (9·0 – 141·0 p.p.m., average 40·6 p.p.m. Rb) is high; while its presence in wines[21-24] is remarkable, up to 4·16 mg./l. occurring in red wines. Rubidium is also found abundantly in the fruiting bodies of certain fungi, such as *Rhodopaxillus*, *Tricholoma* and *Cortinarius*.[25] The highest value found was 2·8 g. Rb/kg. dry weight of *T. album*.

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SECTION LXIII

THE PREPARATION AND USES OF RUBIDIUM

By J.P. QUIN

THE PREPARATION OF RUBIDIUM

In the original Treatise it is stated that although attempts to obtain the metal by the electrolysis of fused rubidium chloride had been unsuccessful, rubidium had been prepared thermally by the reduction of rubidium compounds with calcium, aluminium or magnesium (Mellor,II,447-450). During the last thirty-five years, however, this subject has been studied in considerably greater detail, but it is probably still true to say that the metal is rather a chemical curiosity.

The demand for rubidium, which must have been negligible when Mellor wrote, is still extremely small. In 1946 the world output of the metal in the form of rubidium ore was estimated to be 10 pounds[1] and in 1949 the estimated production of rubidium metal in the United States was 100 g. with an estimated potential output of 1 ton.[2] No later estimates appear to be available. It is evident, however, that production of the metal is limited to very small amounts indeed.

Methods of preparing rubidium have been reviewed by a number of authors.[3-5]

Preparation of Rubidium by Chemical Reaction.

Methods of isolating rubidium by chemical means involve either the thermal decomposition of rubidium compounds or the reduction of such compounds with metallic or non-metallic reducing agents at elevated temperatures. In general the methods yielding sodium metal by chemical reaction are equally applicable to rubidium (see pages 308,324).

Thermal Decomposition of Rubidium Compounds.

Very pure rubidium has been prepared by the thermal decomposition of rubidium azide[6,7] heated at 395°C. under reduced pressure for a period of three to four days. The azide breaks down to give nitrogen and metallic rubidium which distils off in 60% yield and is condensed to give metal which is said to be spectrographically pure and completely free from gaseous impurities.[6-9] When the bluish-green residue remaining after the distillation of the rubidium is treated with water, a considerable quantity of ammonia is evolved, indicating that rubidium nitride has been formed by secondary reaction during the decomposition.[10] The method has the disadvantages that it is slow and that rubidium azide can decompose with explosive violence under certain conditions,[11] so that this method tends to be limited to the production of comparatively small quantities of metal. The formation of rubidium by the thermal decomposition of rubidium cyanate, ferrocyanide or ferricyanide has been considered.[12]

Reduction of Rubidium Compounds with Metallic and Non-metallic Reducing Agents.

The preparation of rubidium by heating a suspension of carbon in molten rubidium hydroxide while passing a stream of inert gas through the melt, and then removing the rubidium vapour so produced from the gas, has been patented.[12a] The reduction of rubidium chloride has been carried out using calcium carbide as the reducing agent. A 75% yield of the metal is obtained when a mixture of rubidium chloride and calcium carbide is heated in vacuo at temperatures of 700–900°C. The condensed metal may be collected in a glass receiver.[13]

According to a patent, rubidium can be prepared by passing the vapour of rubidium chloride over solid calcium carbide in vacuo at 800–1100°C. and condensing the rubidium vapour so formed.[13a]

Barium may be used to reduce rubidium compounds and this method is recommended for the preparation of small amounts of pure rubidium metal. Rubidium chloride is added to an aqueous solution of barium azide and the mixture, after evaporation to dryness, is heated in vacuo. The barium azide decomposes at a temperature between 100° and 200°C. to give metallic barium which in turn reduces the rubidium chloride to rubidium metal.[14] It is essential to carry out the evaporation to dryness at room temperature as at higher temperatures the barium azide may hydrolyze to barium hydroxide, and this tends to reduce the yield of rubidium metal.

One of the most satisfactory methods for preparing rubidium in the laboratory is the Hackspill method whereby rubidium compounds are reduced with metallic calcium.[11] The method has been adopted with minor modifications by a number of workers, and has been extensively used to prepare small amounts of pure rubidium for work on the determination of its physical properties. The original papers may be consulted for details of the apparatus used and the experimental procedure.[15-20] Briefly rubidium chloride and calcium metal are heated under reduced pressure when rubidium distils off as vapour and is suitably condensed. When the rubidium chloride and the calcium are used in stoicheiometric proportions a 50% yield of rubidium is obtained at 900–1000°C.[15] By using an excess of calcium and working under a pressure of 0·02 mm. of mercury, yields of 90–95% may be obtained at temperatures of 500–700°C.[16] The rubidium is freed from excess calcium by distillation at 300°C. under reduced pressure.[16] It is claimed that the Hackspill method gives very pure rubidium: in one case chemical examination of a sample of metal so produced showed no impurities,[17] and another preparation was found to be spectrographically pure rubidium of satisfactory melting point.[18]

The reduction of rubidium compounds with iron has been studied.[12,21] Rubidium is displaced from its compounds by iron more readily than sodium or potassium are from their compounds, provided that the reduction is carried out in vacuo at such a temperature that the vapour pressure of the rubidium is of the order of 1 cm. of mercury or less. Reaction proceeds rapidly at the melting point of the rubidium compounds.

When a mixture of rubidium hydroxide and iron is heated under a pressure of 0·001 mm. of mercury, a slight evolution of hydrogen at 500–550°C. indicates the start of the following reaction:-

$$6RbOH + 4Fe \rightarrow 2Fe_2O_3 + 3H_2 + 6Rb.$$

The reaction goes fairly quickly at 700°C., when the rubidium distils off as vapour and may be condensed. The yield of metal is less than 50%, however, and it has been suggested that this is caused by combination of rubidium hydroxide with the ferric oxide formed during the reduction to give a ferrite which is not reduced under the conditions of the experiment.

When rubidium sulphate is heated with iron under similar conditions a slight evolution of oxygen and sulphur dioxide at 850°C. indicates the start of the reaction, which proceeds rapidly at 1000°C. At 1100°C. an 80% yield of rubidium is obtained. It has also been proposed to prepare rubidium by reducing rubidium carbonate or rubidium nitrate with iron in vacuo at high temperatures.[12]

Iron also reduces rubidium chloride under similar conditions, but the method is not very satisfactory as ferrous chloride volatilizes with the rubidium and on cooling the reverse reaction tends to take place whereby iron and rubidium chloride are formed giving a contaminated product and a reduced yield.[12]

Zirconium powder has been used as a reducing agent to obtain small amounts of pure rubidium for the preparation of pure rubidium compounds.[22-24] When a mixture of rubidium dichromate and zirconium powder in the proportions 1:10 is heated in vacuo at 370°C., rubidium free from oxide is obtained in 80–90% yield.[22] Using rubidium chromate and zirconium in the proportions 1:4 the reaction starts at 700°C. in vacuo, and rubidium distils over in almost a quantitative yield.[22]

The preparation of rubidium by the reduction of rubidium compounds with reducing agents such as aluminium and silicon,[15] hafnium or titanium,[26] thorium[27] and cadmium,[28] has been patented. Rubidium may also be prepared directly from rubidium ores such as the silicate or phosphate. Thus, a patent describes the recovery of the metal by direct distillation from a pelleted mixture of ore with excess of lime and a reducing agent such as aluminium, silicon or ferrosilicon, under a pressure not exceeding 1 mm. of mercury at temperatures above 900°C.[29]

ELECTROLYTIC PREPARATION OF RUBIDIUM

Little work has been done on the preparation of rubidium by the electrolysis of rubidium compounds in solution in non-aqueous solvents. According to a patent rubidium is prepared by the electrolysis of a non-aqueous liquid comprising anhydrous liquid ammonia, methylamine, ethylamine, pyridine or mixtures of these liquids, and containing a solution of a rubidium salt such as the perchlorate or thiocyanate. Iron, copper or carbon may be used for the cathode, and carbon is the preferred anode material. The concentration of the rubidium salt in the anhydrous liquid must be at least 2 g.-mol./litre. The rubidium is deposited as liquid solution, paste, or metal depending on the concentration of the rubidium salt in the electrolyte. It is stated that the deposited metal can be readily separated from the electrolyte, substantially free from unelectrolysed salt.[29a] Rubidium is formed by the electrolysis of solutions of mixtures of rubidium bromide and aluminium bromide in nitrobenzene. To obtain satisfactory results, it is desirable to use a diaphragm and to operate at a low current density.[30,31] The Ewan process, whereby a solution of an alkali metal salt in liquid ammonia is electrolyzed in the presence of an alkali amalgam anode, has been proposed for the preparation of rubidium.[32] The extraction of rubidium from rubidium amalgam by leaching with inert solvents such as liquid ammonia, ethylenediamine or methylamine, followed by evaporation of the solvent to recover the metal, has been considered.[33,33a,33b]

There is also little information on the electrolysis of fused rubidium compounds. According to a patent,[34] the efficiency of electrolysis of fused rubidium hydroxide is likely to be increased by carrying out the electrolysis in the presence of fused rubidium amide (see also page 337). Similar results may be expected when rubidium nitrate is electrolyzed in the presence of auxiliary salts such as rubidium amide or rubidium carbonate.

The development of a miniature cell, designed for the preparation of small amounts of alkali metals by electrolysis of their fused salts, has been described.[35] The electrolysis is carried out in a carbon container which also serves as the anode, using a stainless steel cathode and an alundum diaphragm. The method is particularly recommended for the preparation of small amounts of metal from isotopic compounds, and it is suggested that it may be applicable to the production of rubidium, but no attempt has actually been made to prepare rubidium in this way.

PURIFICATION OF RUBIDIUM

Rubidium, like the other alkali metals, is readily purified by distillation in vacuo, and the necessary procedure has been described in detail by several authors.[36-40] The purification of alkali metals such as rubidium by treatment of the metal with molten rubidium chloride or other molten inert salts has been patented.[41]

HANDLING AND STORAGE

The handling and storage of rubidium have been discussed.[42] The metal may be handled as described for sodium (see page 362). Consideration must be given, however, to the fact that rubidium will ignite spontaneously when exposed to air.[42]

A technique for the preparation of samples of rubidium suitable for the determination of physical properties has been described[42a] and the preparation of colloidal rubidium has been discussed.[42b,42c]

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THE USES OF RUBIDIUM

The uses of rubidium are very limited. The metal may be used to remove the last traces of air from vacuum tubes and to obtain high vacua in radio valves.[1,2] The chief application, however, appears to be in the manufacture of photoelectric cells, and it is claimed that rubidium is more suitable than cæsium for this purpose because, when the former metal is used, a thinner layer can be deposited on the light-sensitive cathode.[3-10] Rubidium may be introduced into the cell in excess, and removed at a later stage, except for a monomolecular layer of rubidium oxide which is formed on the silver or base metal electrode.[3] Alternatively the rubidium may be produced in situ by the reduction of a rubidium compound with a suitable reducing agent[6] or by the electrolytic decomposition of a rubidium compound.[4] Rubidium contains ^{87}Rb which is radioactive and this is discussed in detail in a later Section (see page 2492). As yet no commercial use appears to have been made of this property of the metal.[9]

The radioactive isotope ^{86}Rb has however been used for the detection of slag in steel sheets or plates,[11] and to determine retention times in sedimentation basins and filters.[12]

The use of sodium–rubidium alloys as coolants in thermal piles has been discussed.[13]

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SECTION LXIV

THE PHYSICAL PROPERTIES OF RUBIDIUM

By W. H. WILSON

Structure, atomic and ionic radii, etc.

Rubidium crystallizes as a body-centred cube both at ordinary and at low temperatures.[1-5] Its lattice constant at 291°K. was found by Hume-Rothery and Lonsdale[6] to be 5·699 kX. (equivalent to 5·710 A.), whilst in another study[7] employing *X*-ray reflections extending to larger Bragg angles a lattice constant of 5·697 A. to 5·700 A. was obtained at 297°K. These results correspond to a room-temperature atomic radius of 2·47 A. At 90°K. the above two investigations gave lattice constants of 5·624 kX. (equivalent to 5·635 A.)[6] and 5·616 to 5·619$_5$ A.[7] Values recorded for the lattice constant of rubidium at other temperatures include 5·607 to 5·613 A. at 77°K.,[7] 5·62 A. at 90°K.,[1,2] and 5·66 A. at 263°K.[5]

Metallographic examination at 0°C. of 99·9% rubidium specimens cooled previously to 1·2°K. has shown no trace of a spontaneous, low-temperature, martensitic transformation similar to that observed with lithium and sodium (see Part I, pages 32 and 377).[8]

Bidwell[9] observed a break in the thermoelectric power–temperature curve of rubidium in the region of −30°C. and assumed it to indicate a transformation from a crystalline form to an amorphous form. Other measurements[10] have shown the presence of a break in the variation of resistance with temperature at about 180°K., but microscopical examination of rubidium surfaces in the neighbourhood of this 'transition' temperature and at temperatures down to 77°K. has shown no signs of a structural change.[7] It seems probable that some change in electronic configuration occurs.[10]

In an experiment in which rubidium was subjected to high pressure at low temperatures, Swenson[11] heard a sharp crack and noted a 10% volume decrease at a pressure of several hundred atmospheres. On warming to room temperature, the density of the resulting sample was 1·71 g./c.c. as against 1·53 g./c.c. for normal rubidium. The sample showed no evidence of melting at 100°C. (normal m.p. ~ 39°C.), but following this heating there was a slight decrease in density. This behaviour was not reproduced in two other runs, but the isolated and unexplained result was reported as possibly indicating a new, high density, form of rubidium stable at room temperature.

The diffraction of *X*-rays by liquid rubidium has been studied by Randall and Rooksby[12] who found an intensity peak at $(\sin\theta)/\lambda = 0{\cdot}122$.

Several authors have given theoretical treatments of the cohesion in metallic rubidium and have calculated the usual solid state parameters.[13-18] Gombas[14,16] has applied his statistical model (see page 1503) to the problem, while Kuhn and Van Vleck[17] have employed their method which permits the evaluation of the cohesive energy and lattice constant without the computation of a central field for the atom.

Pauling[19] made use of five experimental interionic distances, namely those in NaF, KCl, RbBr, CsI and Li_2O, to construct a set of ionic radii in which the rubidium ion had a radius of 1·48 A. An earlier treatment by Goldschmidt[19a] gave 1·49 A. for the radius of the Rb^+ ion. Other works[19,20] may be consulted for details of these and other earlier treatments.

Density and thermal expansion

Values of 1·522 at 15°C.[21] and 1·5218 at 18°C.[22] have been reported for the density of solid rubidium. Other work[11] has given 1·53 at room temperature. *X*-Ray measurements[6,7] lead to 1·525 to 1·535 for the density at room temperature. Low temperature measurements have given the density as 1·64 at 77°K. and 1·63 at 4·2°K.[11] The density at 100°K. as calculated from *X*-ray measurements is 1·59 and the value at 0°K. has been given as 1·61.[1,2] The possible existence of a high density form of rubidium ($d_{300°K.}$ = 1·71; $d_{77°K.}$ = 1·79) has been reported[7] (see page 2144).

Andrade and Dobbs[23] obtained 1·472 ± 0·001 g./cm.³ for the density of liquid rubidium at its melting point (39°C.), a value in close agreement with that of 1·475 g./cm.³ obtained much earlier by Hackspill.[24] But other measurements[25,26] from the melting point up to 400°C. have been represented by the equation:

$$d(\text{g./cm.}^3) = 1{\cdot}52 - 0{\cdot}00054\,(t(°\text{C.}) - 39)$$

which corresponds to 1·52 g./cm.³ for the density at the melting point. Although measurements were made only to 400°C., the belief has been expressed[25] that this equation is satisfactory up to the boiling point (688°C.).

The increase in volume on fusion has been reported as 2·57%[21] and as 2·54%[22] or 0·0172 cm.³/g. Other measurements[27,28] of the volume increase on fusion at pressures up to 3,500 kg./cm.² are:

Pressure, kg./cm.²	ΔV, cm.³/g.
1	0·0185
500	0·0163
1000	0·0145
1500	0·0130
2000	0·0119
2500	0·0112
3000	0·0106
3500	0·0101

Dilatometric measurements of the thermal expansion of rubidium between 120 and 295°K. have shown the coefficient of expansion to be largely independent of temperature.[7] Some experiments, however, indicated a sudden change in the value at a temperature between 150 and 210°K., but other runs did not show this behaviour. The ratio of the expansion coefficients above and below this break (when observed) was 4·7, and the absolute coefficients have been estimated, with an uncertainty of 40%, as 3×10^{-4} above the transition and 6×10^{-5} below it. *X*-Ray measurements[6] have led to $6{\cdot}6 \times 10^{-5}$ for the coefficient of expansion between 176° and 292°K.; other *X*-ray studies[7] have shown this value to be acceptable over the range 77° to 300°K.

Mechanical properties

The effect of pressures up to 100,000 kg./cm.² on the volume of rubidium has been studied by Bridgman;[27-36] Table I is based on his more recent work.[32,33]

Figure 1 (see page 2295) compares the behaviour of the five alkali metals under pressure. A study[11] of the compression of the alkali metals at low temperatures has given the figures in Table II for the relative volume of rubidium at 4·2°K. (1 atm. = 1·033 kg./cm.²).

TABLE I.- EFFECT OF PRESSURE ON THE VOLUME OF RUBIDIUM AT ROOM TEMPERATURE

Pressure, kg./cm.^{2}	Relative Volume	Pressure, kg./cm.^{2}	Relative Volume
0	1·0	40,000	0·612
2,500	0·970	50,000	0·578
5,000	0·878	60,000	0·551
10,000	0·801	70,000	0·528
15,000	0·749	80,000	0·507
20,000	0·708	90,000	0·489
25,000	0·675	100,000	0·473
30,000	0·652		

TABLE II.- EFFECT OF PRESSURE ON THE VOLUME OF RUBIDIUM AT 4·2°K.

Pressure, Atmospheres	Relative Volume	Pressure, Atmospheres	Relative Volume
0	1·000	3,000	0·916
500	0·984	4,000	0·894
1,000	0·969	6,000	0·858
1,500	0·954	8,000	0·829
2,000	0·940	10,000	0·804

Bridgman[27] gave the initial compressibility of rubidium at 50°C. as 52×10^{-12}cm.^{2}/dyne. More recent values[11] for the initial compressibility at low temperatures are $38{\cdot}3 \times 10^{-12}$cm.^{2}/dyne at 77°K. and $34{\cdot}3 \times 10^{-12}$cm.^{2}/dyne at 4·2°K. Measurements of the velocity of ultrasonic waves in liquid rubidium (page 2160) have given $42{\cdot}7 \times 10^{-12}$cm.^{2}/dyne for the adiabatic compressibility of the liquid at its melting point and $49{\cdot}1 \times 10^{-12}$cm.^{2}/dyne for the isothermal compressibility at the same temperature.[37]

Surface properties and colloidal rubidium

No experimental determinations of the surface tension of rubidium appear to have been carried out, but with the aid of values for other physical properties the surface tension of liquid rubidium at its melting point has been estimated as 75 dynes cm.$^{-1}$.[38] From a consideration of the co-ordination numbers of atoms at the surface and in the bulk of the liquid, 100 dynes cm.$^{-1}$ has been calculated for the surface tension.[39]

Various wave mechanical calculations[40-43] of the surface tension of rubidium have given widely differing values (50 to 140 dynes cm.$^{-1}$); the treatment[43] that achieved closest agreement with experiment in the case of lithium, sodium and potassium gives 50 dynes cm.$^{-1}$ for the surface tension of rubidium at its melting point.

Liquid rubidium wets and adheres to glass.[7] This has been the cause of difficulties in the determination of certain physical properties at low temperatures.[7] Deformation of the metal may occur on cooling because of the adhesion and so give rise to variable results.

From surface tension values for fused salts and for salts in solution the atomic parachor of rubidium has been calculated as 130[44] and 141·62[45] respectively.

Rubidium dispersions may be prepared by the method that has been widely applied in the case of sodium (Part I, p. 386), namely by agitating the molten metal with the dispersion medium and continuing agitation whilst cooling until the metal particles have solidified. Dispersions of rubidium in mineral oil prepared by this technique are reported not to coagulate even when heated above the melting point of the metal.[46]

Colloidal solutions of rubidium have been prepared by evaporating the metal and the dispersion medium in a vacuum, condensing the mixed vapours on a surface cooled with liquid air, and then warming to room temperature.[47,48] Rubidium sols in ether prepared in this way by Tomashevskii had a dark blue colour and were stable for only twenty minutes.[48]

Viscosity

By the use of an oscillating sphere method, the figures of Table III have been obtained for the viscosity of rubidium.[23]

TABLE III.- VISCOSITY OF RUBIDIUM

Temp. °C.	Viscosity millipoise
38·0	6·734
39·0	6·713
40·0	6·663
45·0	6·441
50·0	6·258
99·7	4·844
140·5	4·133
179·0	3·634
220·1	3·234

These data have been represented by the equations:

$$\eta = 9{\cdot}27 \times 10^4 e^{617/T}$$

and

$$\eta v^{1/3} = 1{\cdot}023 \times 10^3 e^{371/vT}$$

v being the specific volume. The latter equation, which makes allowance for the change of volume with temperature, gives the slightly closer fit.

Melting point and heat of fusion

The samples of rubidium used by most investigators have contained small amounts of other alkali metals as impurity. As a consequence the observed melting points tend to be rather lower than the true value. Amongst the higher values reported are 38·8°C.,[22] 38·7°C.[27,28] and 38·5°C.,[21] and the best rounded representative value for the melting point is probably still that of 39°C. quoted previously (Mellor, II, 457). Some recent measurements[49] indicate, however, that the true value may be around 40°C.

At pressures up to 135 atm. the melting point has been determined as:[22]

Pressure, atm.	m.p., °C.
1	38·8
50	39·8
100	40·9
135	41·6

Measurements at higher pressures have given the values shown on the next page[27,28] (1 atm.≡1·033 kg./cm.^{2}).

Comparison with the other alkali metals is made in Fig. 2, page 2298.

A value[49] of approximately 540 g.-cal./g. mole (equivalent to 6·3 g.-cal./g.) has been obtained for the latent heat of fusion of rubidium. This agrees fairly well with earlier values[50,51] of about 6·1 g.-cal./g.

Pressure kg./cm.^{2}	m.p., °C.
1	38·7
500	48·7
1000	57·9
1500	66·5
2000	74·5
2500	82·0
3000	89·1
3500	95·9

From experimental data for the variation of melting point with pressure and the volume change on fusion, the Clapeyron equation has yielded values of 6·2 to 6·5 g.-cal./g. for the latent heat of fusion of rubidium at pressures of 1 to 3500 kg./cm.^{2}.[27,28]

Vapour pressure, boiling point, and degree of association

Measurements of the vapour pressure of liquid rubidium were made by Scott[52] over the range 364° to 400° K. using a vibrating quartz fibre manometer; his results can be represented by the equation:

$$\log_{10} p \text{ (mm.)} = -4209/T + 7{\cdot}331$$

From measurements of the ion current from a tungsten filament in rubidium vapour at various temperatures Killian[53] obtained values for the vapour pressure of rubidium between 310° and 380° C. that can be represented by the equation:

$$\log_{10} p \text{ (mm.)} = -4132/T + 7{\cdot}43$$

Killian's values were approximately double those obtained by Scott. Ditchburn and Gilmour[54] in reviewing vapour pressure data in 1941 gave the equation:

$$\log_{10} p \text{ (mm.)} = -4302/T - 1{\cdot}5 \log_{10} T + 11{\cdot}722$$

to represent the vapour pressure of rubidium between 325° and 600° K. with an accuracy of ±20%, the equation being constructed to fit the results of Killian[53] and the older values of Hackspill.[55] Temperatures at which the vapour pressure assumes rounded values as calculated from this equation are given in Table IV.[54]

TABLE IV.- VAPOUR PRESSURE OF RUBIDIUM

Pressure, mm. Hg	T, °K.
10^{-6}	(310)
10^{-5}	332
10^{-4}	362
10^{-3}	397
10^{-2}	441
10^{-1}	495
10^{0}	567
10^{1}	(660)

By extending the equation[54] to higher pressures and temperatures a value of 990° K. is obtained for the boiling point of rubidium. From other vapour pressure equations a boiling point of 974° K. has been obtained.[56]

From spectroscopic data the values of Table V have been calculated for the dissociation constant of diatomic rubidium vapour into atoms[57] (partial pressures in atmospheres).

TABLE V.- DISSOCIATION CONSTANT FOR DIATOMIC RUBIDIUM VAPOUR

T, °K.	Log K = Log$(P_{Rb})^2/P_{Rb_2}$
273·16	−5·703
298·16	−4·922
400	−2·740
600	−0·589
800	+0·501
1000	+1·161
1200	+1·606
1400	+1·925
1500	+2·054

The dissociation energy, D_0^0, of the Rb_2 molecule, as calculated from spectroscopic data, lies in the vicinity of 0·47 to 0·49 e.V. (equivalent to 10·8 to 11·3 kg.-cal./g.mole).[58,59,60] Gaydon[61] lists 0·47 ± 0·05 e.V. as the best value, while Herzberg[62] gives 0·49 e.V. The U.S. Bureau of Standards selected value[63] for the heat of formation of the gaseous Rb_2 molecule at 298·16°K. is 29·6 kg.-cal./g.-mole. Values for the heat and free energy of formation of diatomic rubidium vapour from the monatomic vapour are included in Table IX (page 2151).

Heats of vaporization and sublimation

Using largely the vapour pressure data of Scott,[52] Kelley[64] represented the heat of vaporisation of rubidium by the equation:

$$\Delta H \text{ (kg.-cal./g.-atom)} = 20{\cdot}850 - 2{\cdot}88 \times 10^{-3} T$$

and the free energy of vaporisation by:-

$$\Delta F \text{ (kg.-cal./g.-atom)} = 20{\cdot}850 - 6{\cdot}63 \times 10^{-3}\, T \log T - 4{\cdot}164 \times 10^{-2} T.$$

At the boiling point (which Kelley took as 952°K.), ΔH becomes 18·108 kg.-cal./g.-atom and ΔS is 19·0 g.-cal./g.-atom, whilst

$$\Delta H_{298\cdot1} = 19{\cdot}991 \text{ kg.-cal./g.-atom and } \Delta F^0_{298\cdot1} = 13{\cdot}327 \text{ kg.-cal./g.-atom.}$$

For the heat and free energy of sublimation Kelley[64] has given the following equations:

$$\Delta H \text{ (kg.-cal./g.-atom)} = 20{\cdot}580 + 1{\cdot}70 \times 10^{-3} T - 6{\cdot}55 \times 10^{-6} T^2$$

$$\Delta F \text{ (kg.-cal./g.-atom)} = 20{\cdot}580 - 3{\cdot}92 \times 10^{-2} T \log T + 6{\cdot}55 \times 10^{-6} T^2 - 1{\cdot}650 \times 10^{-2} T$$

which lead to $\Delta H_{298\cdot1}$ = 20·505 kg.-cal./g.-atom, $\Delta F^0_{298\cdot1}$ = 13·352 kg.-cal./g.-atom, and $\Delta S_{298\cdot1}$ = 24·0 g.-cal./g.-atom.

The U.S. Bureau of Standards selected values[63] for the heats, free energies and entropies of vaporisation and sublimation are based on the above equations of Kelley. More recent calculations[56] have given the heat of sublimation at 298°K. as 19·6 kg.-cal./g.-atom to monatomic gas and as 27·55 kg.-cal./g.-atom to diatomic gas. It was taken that the total pressure reached one atm. at 974°K., and at this temperature the heat of vaporisation to the equilibrium gas was calculated to be 16·54 kg.-cal./g.-atom.

Specific heat, enthalpy and entropy

Values for the specific heat of rubidium below 300°K. are shown in Table VI.[49] At temperatures below about 225°K. an anomalous behaviour has been

TABLE VI.- SPECIFIC HEAT OF RUBIDIUM AT CONSTANT PRESSURE

T, °K.	C_p, g.-cal./g.-mole	T°K.	C_p, g.-cal./g.-mole
25	4·49	140	6·30
30	4·90	160	6·41
35	5·15	180	6·48
40	5·35	200	6·57
50	5·58	220	6·65
60	5·76	240	6·78
70	5·87	260	6·94
80	5·97	273·15	7·06
90	6·06	280	7·26
100	6·14	298·15	7·38
120	6·19	300	7·42

observed, the specific heat–temperature curve showing some small irregularities.[49] The exact behaviour in the anomalous region depends on the thermal history of the specimen, and, in particular, is affected by heating the specimen above its melting point. As with the other alkali metals there is a marked increase in specific heat as the melting point is approached. For the liquid immediately above the melting point the specific heat has a value of approximately 7·7 g.-cal./g.-mole.

Kelley[65] in a review of thermal data up to 1948 made use of the much older measurements of Deuss[50] and of Rengade[51] to obtain the following equations for the enthalpy or heat content (in g.-cal./g.-mole) of solid and liquid rubidium:

Solid: $H_T - H_{298\cdot16} = 7\cdot27\,T - 2{,}168$ (2% accuracy between 298° and 312·2° K.)

Liquid: $H_T - H_{298\cdot16} = 7\cdot80\,T - 1{,}808$ (3% accuracy between 312·2° and 400° K.)

These correspond to 7·27 kg.-cal./mole for the specific heat of the solid and to 7·80 kg.-cal./mole for that of the liquid. Table VII shows thermodynamic functions for solid and liquid rubidium from a compilation by Stull and Sinke[56] in 1956. An average heat capacity of 7·5 g.-cal./g.-atom was estimated for the liquid range. From low-temperature heat capacity measurements (Table VI)[49] the enthalpy and entropy of the solid at 298° K. were calculated[56] as 1790 g.-cal./g.-atom and 18·22 g.-cal./g.-atom/degree respectively.

TABLE VII.- THERMODYNAMIC FUNCTIONS FOR SOLID AND LIQUID RUBIDIUM

T, °K.	$C_p°$ g.-cal./ g.-atom/deg.	$H°_T - H°_{298\cdot15}$ g.-cal./g.-atom	$S°_T$ g.-cal./g.-atom/deg.	$-(F°_T - H°_{298\cdot15})/T$ g.-cal./g.-atom/deg.
298	7·50	0	18·22	18·22
300	7·55	14	18·27	18·23
400	7·50	1324	22·22	18·91
500	7·50	2074	23·90	19·76
600	7·50	2824	25·26	20·56
700	7·50	3574	26·42	21·32
800	7·50	4324	27·42	22·02
900	7·50	5074	28·30	22·67

Using vapour pressure data and his value for the entropy of rubidium vapour (see below), Kelley[64,66] computed 16·6 g.-cal./g.-atom/degree for the entropy of solid rubidium at 298·16° K. This was taken as the U.S. Bureau of Standards selected value[63] in 1952.

From vibration frequency data, Kelley[65] represented the heat content (in g.-cal./g.-mole) of diatomic rubidium vapour by the equation:

$$H_T - H_{298\cdot16} = 8\cdot95T + 0\cdot02 \times 10^5 T^{-1} - 2,676$$

(1% accuracy between 298° and 2000° K.).

It follows that the specific heat of the diatomic vapour is:

$$C_p = 8\cdot95 - 0\cdot02 \times 10^5 T^{-2}$$

Recent calculations[57] using spectroscopic data have given the selection of values for the thermodynamic properties of monatomic and diatomic rubidium vapour shown in Table VIII and Table IX respectively. Other calculations[67] of free energy functions are in close agreement with those of Table VIII.

TABLE VIII.- THERMODYNAMIC PROPERTIES OF MONATOMIC RUBIDIUM VAPOUR

T, °K.	$-(F^\circ-H^\circ_0)/T$ g.-cal./g.-atom/°K.	$(H^\circ-H^\circ_0)/T$ g.-cal./g.-atom/°K.	S° g.-cal./g.-atom/°K.	$C_p{}^\circ$ g.-cal./g.-atom/°K.
50	26·7896	4·9680	31·7576	4·9680
100	30·2331	4·9680	35·2011	4·9680
250	34·7852	4·9680	39·7532	4·9680
273·16	35·2254	4·9680	40·1934	4·9680
298·16	35·6604	4·9680	40·6284	4·9680
400	37·1202	4·9680	42·0882	4·9680
500	38·2288	4·9680	43·1968	4·9680
600	39·1345	4·9680	44·1025	4·9680
800	40·5637	4·9680	45·5317	4·9680
1000	41·6723	4·9680	46·6403	4·9680
1200	42·5781	4·9680	47·5461	4·9683
1400	43·3439	4·9682	48·3121	4·9701
1500	43·6866	4·9684	48·6550	4·9724
1600	44·0074	4·9687	48·9761	4·9764
1800	44·5926	4·9703	49·5629	4·9920
2000	45·1164	4·9739	50·0903	5·0227
2200	45·5908	4·9805	50·5713	5·0743
2400	46·0246	4·9914	51·0160	5·1520
2500	46·2285	4·9988	51·2273	5·2021

TABLE IX.- THERMODYNAMIC PROPERTIES OF DIATOMIC RUBIDIUM VAPOUR

T, °K.	$-(F^\circ-H^\circ)/T$ g.-cal./g.-mol./°K.	$(H^\circ-H^\circ_0)/T$ g.-cal./g.-mol./°K.	S° g.-cal./g.-mol./°K.	$C_p{}^\circ$ g.-cal./g.-mol./°K.	$-\Delta H_f{}^\circ$* kg.-cal./mole	$-\Delta F_f{}^\circ$* kg.-cal./mole
0	0	0			11·30	11·30
250	54·408	8·688	63·096	9·034	11·612	7·509
273·16	55·179	8·718	63·897	9·048	11·633	7·128
298·16	55·944	8·746	64·690	9·061	11·655	6·715
400	58·527	8·833	67·360	9·111	11·741	5·015
500	60·505	8·893	69·398	9·158	11·822	3·324
600	62·13	8·94	71·07	9·20	11·90	1·62
800	64·71	9·02	73·73	9·29	12·03	−1·83
1000	66·73	9·08	75·81	9·38	12·16	−5·31
1200	68·39	9·14	77·53	9·47	12·26	−8·82
1400	69·81	9·19	79·00	9·56	12·34	−12·33
1500	70·44	9·22	79·66	9·60	12·38	−14·10

* The reference state in computing the heat and free energy of formation is taken as the monatomic gas.

Refs. p. 2160

Using the Sackur equation, with $R\ln 2$ added to account for the multiplicity in the lowest energy state, Kelley[66] obtained 40·64 ± 0·01 g.-cal./g.-atom/degree for the entropy of monatomic rubidium vapour at 298·16°K. For diatomic rubidium vapour the same author[66] estimated $S^{\circ}_{298\cdot16}$ = 63·1 ± 1·5 g.-cal./g.-mole/degree.

Thermal conductivity

Thermal conductivities of rubidium between 2° and 70°K. have been measured by MacDonald *et al.*[68] (see Fig. 1). Between 24°K. and 70°K. the conductivity fell only from 0·65 watt cm.$^{-1}$ degree^{-1} to 0·62 watt cm.$^{-1}$ degree^{-1}. Below 8°K. its value in watt cm.$^{-1}$ degree^{-1} is given by

$$1/_{\kappa} = 1{\cdot}50/_{T} + 9{\cdot}3 \times 10^{-3}T^2$$

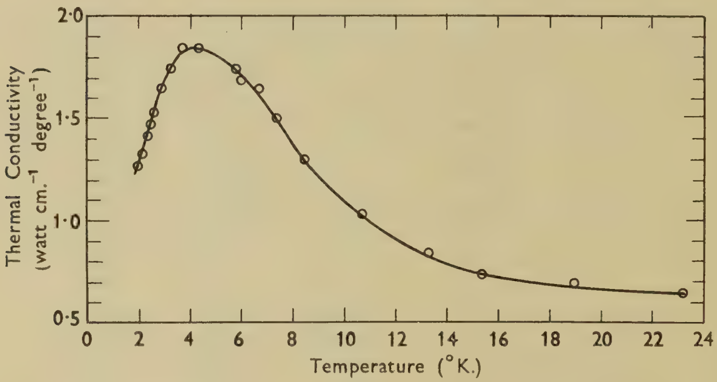

FIG. 1. THERMAL CONDUCTIVITY OF RUBIDIUM AT LOW TEMPERATURES

By combining relative values[69] for the thermal conductivities of sodium, potassium and rubidium with other measurements[70] of the conductivities of sodium and potassium, values of 0·07 and 0·075 g.-cal. cm.$^{-1}$ sec.$^{-1}$ degree^{-1} (equivalent to 0·29 and 0·31 watt cm.$^{-1}$ degree^{-1}) have been calculated for the thermal conductivity of liquid rubidium at its melting point and at 50°C. respectively.[71] Employing the relationship between electrical and thermal conductivity - the Lorenz number - the thermal conductivity of liquid rubidium at its melting point has been estimated as 0·085 to 0·11 g.-cal. cm.$^{-1}$ degree^{-1} (equivalent to 0·36 to 0·46 watt cm.$^{-1}$ degree^{-1}).[72]

Electrical resistance

A number of determinations[9,10,68,73-78] have been made of the ratio of the electrical resistance of rubidium at various temperatures, but little attention has been paid to its specific resistance. One measurement[68] of the specific resistance at 22°C. has given 14·6 × 10^{-6} ohm cm. Table X shows values of the $R/R_{0^{\circ}\mathrm{C.}}$ ratio interpolated from measurements by MacDonald,[10] and also values obtained similarly from the earlier measurements of Bidwell.[9]

TABLE X.- RELATIVE ELECTRICAL RESISTANCE OF RUBIDIUM

Temp., °C.	−250	−200	−150	−100	−50	0	+50	+100	+150
$R/R_{0^{\circ}\mathrm{C.}}$ (Ref. 10)	0·12	0·28	0·42	0·56	0·79	1·0	-	-	-
$R/R_{0^{\circ}\mathrm{C.}}$ (Ref. 9)	-	-	0·38	0·56	0·76	1·0	2·0	2·4	2·7

MacDonald[10] found a marked break in the plot of $R/R_{0°C.}$ against temperature at about 180°K., but this does not correspond to a structural change (see page 2144). Rubidium samples allowed to stand at rather higher temperatures (~ 200°K.) undergo a gradual decrease in resistance with time.[10]

The temperature region below about 20°K. has been extensively investigated:[10,68,73-78] only below temperatures of a few degrees K. does the resistance of rubidium, after correcting for the residual resistance, show a fifth power dependence on temperature.[68,77] Below 5°K. the resistivity, less the residual resistivity, has been represented by[68]

$$\rho(\text{ohm cm.}) = 6{\cdot}8 \times 10^{-12}T^5$$

As with the other alkali metals, there is a large increase in the resistance of rubidium as the melting point is approached.[9]

By directing a beam of rubidium atoms on to a cooled glass surface, a thin rubidium film can be formed which exhibits an electrical conductivity before the number of atoms deposited is sufficient for a monatomic layer.[79,80] With increasing thickness the resistance and resistivity of the film decrease, but on stopping deposition the film gradually breaks up and the resistance increases. The behaviour is very sensitive to the surface condition of the substrate, and if small amounts of impurity are present a much thicker film is required before conductivity is exhibited; also the rate of decay of conductivity increases. Fig. 3 on page 1518 compares the formation and decay of conductivity for films of rubidium, potassium and cæsium deposited at 90°K. with approximately the same beam intensity in each case.[81] For rubidium, conductivity began at a film thickness of around 2·8 A. and at a thickness of 20 A. the resistivity was about 4,700 times that of the bulk metal. Decay of conductivity after cessation of deposition decreased with increasing film thickness and with decreasing temperature. At 64°K. a film 43·6 A. thick was completely stable and its resistivity was about 10 times that of the bulk metal: a film 90 A. thick had a resistivity only 5 to 6 times that of the bulk metal. Whilst such films are still invisible, a 1·5 cm. square patch is reported to carry a current of half an ampere, the only limitation being in the heating of the end contacts.[79] The resistivity of these thin films has been the subject of theoretical treatment.[82] In films almost 10^4 A. thick the resistivity is still higher (~50%) than in the bulk metal, but the temperature coefficient is the same.[83] Whilst for film thicknesses below 100 A. the greatly increased resistivity is attributed to limitation of the mean free path of the conduction electrons by the boundaries of the film, for the thicker films the increased resistivity is attributed to lattice strain.[83]

The conductivity of thin alkali metal films, probably monatomic, deposited spontaneously on the glass walls of vessels containing the metal in vacuo has been found to increase in the order K, Rb, Cs.[84]

At 14°K., Justi[76] found no significant increase in the electrical resistance of rubidium on application of a transverse magnetic field of 40 kilogauss. Other measurements of the magneto-resistive effect in rubidium at low temperatures have been made by MacDonald.[85]

Measurements of the effect of pressure on the electrical resistance of rubidium have been made by Bridgman[86-88] up to higher and higher pressures as new experimental techniques have been developed. Table XI[86] shows the results of measurements at 30°C. made in 1930 up to 20,000 kg./cm.². A minimum resistance occurred at 17,000 kg./cm.². Measurements[87] made in 1938 up to 30,000 kg./cm.² gave the minimum resistance at 15,000 kg./cm.², but the earlier values were preferred since these were obtained on a bare wire whereas the later measurements were made in glass. More recently[88] when the range of the measurements was extended to 100,000 kg./cm.² (Table XII) the minimum resistance was found near 20,000 kg./cm.².

TABLE XI.- EFFECT OF PRESSURES UP TO 20,000 kg./cm.² ON THE ELECTRICAL RESISTANCE OF RUBIDIUM

Pressure kg./cm.² × 10³	$R/R_{\text{zero pressure}}$
0	1·0
2·5	0·656
5·0	0·504
7·5	0·416
10·0	0·364
12·5	0·333
15·0	0·316
17·5	0·310
20·0	0·314

TABLE XII.- EFFECT OF PRESSURES UP TO 100,000 kg./cm.² ON THE ELECTRICAL RESISTANCE OF RUBIDIUM

Pressure, kg./cm.² × 10³	$R/R_{\text{zero pressure}}$
0	1·0
10	0·326
20	0·309
30	0·455
40	0·695
50	0·925
60	1·218
70	1·594
80	1·972
90	2·38
100	2·95

Thermoelectric properties

Bidwell[9] measured the thermoelectric power of rubidium relative to platinum between −180° and +150°C. (Fig. 2). There is a break in the curve at

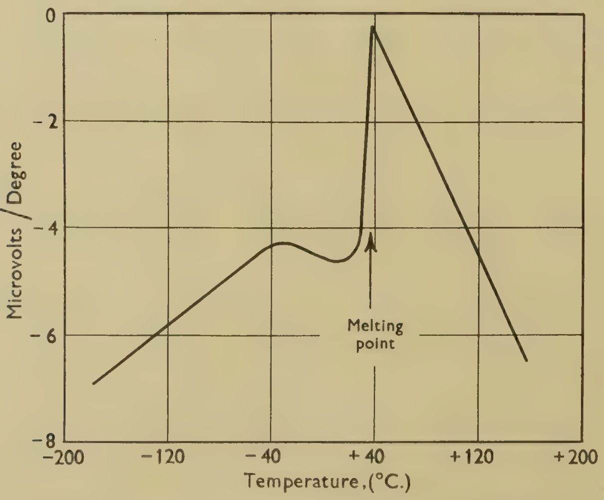

FIG. 2. THERMOELECTRIC POWER OF RUBIDIUM

about −30°C. and a marked increase in thermoelectric power as the melting point is approached. The thermoelectric power of the liquid decreases with increasing temperature. Other measurements of thermoelectric power against platinum showed no discontinuity in the region of 180°K. where a sharp 'transition' in electrical resistance was observed, although there was a gradual change in slope and hence a change in the Thomson coefficient.[7] Thermoelectric force measurements against lead over the range from 4·2°K. to ~300°K. have shown no anomaly in the region of the resistive 'transition'.[7] Using the absolute thermoelectric force of lead as measured by Borelius *et al.*,[89] the following values (interpolated from graphically presented results) have been obtained for the absolute thermoelectric force of rubidium.[90] There is a change in sign of the thermoelectric power around 16°K.:[90]

Temperature, °K.	5	10	20	30	40	50	60
Microvolts	0	4	7	2	−7	−22	−42

Magnetic properties

Rubidium is paramagnetic, its susceptibility varying only slightly with temperature. Room temperature determinations of the mass susceptibility have given 0·21 × 10^{-6},[91,92] 0·225 × 10^{-6},[5] and 0·228 ± 0·002 × 10^{-6}.[93] Sucksmith,[94] who reported a much lower room temperature susceptibility of 0·07 × 10^{-6}, found that the susceptibility increased by about 0·02 × 10^{-6} as the melting point was approached, decreased again when the metal became molten, and then increased slightly with increasing temperature to 0·11 × 10^{-6} at 500°C. Böhm and Klemm[5] have given the following figures for the atomic susceptibility (mass susceptibility × atomic weight) between −183° and +100°C.:-

Temperature, °C.	−183	−78	+20	+100
$\chi_{At} \times 10^6$	21·5	21·5	19·2	18·2

A value[95] of −7·0 × 10^{-6} for the atomic susceptibility is out of line with the results of all subsequent workers.

Theoretical treatments of the magnetic susceptibility of rubidium have appeared.[96,97]

There have been numerous attempts to evaluate the contribution of the rubidium ion to the diamagnetism of its salts starting both from purely theoretical considerations and from experimental data on the susceptibility of salts. Values for the susceptibility of the rubidium ion in solution, obtained from measurements on its salts, include −31·3,[98] −25·0,[99] −24·0,[100] −23·0[101,102] (all to be multiplied by 10^{-6}), while values for the Rb^+ ion in crystals include −29·9,[95] −27·2,[103] and −22·0[104,105] (all to be multiplied by 10^{-6}). Theoretical treatments have given the following values for free rubidium ions: −35,[106] −32,[107] −30·12,[108] −28·0,[109] −27·8,[110] −27·5,[111] −25·8,[112] and −24·05[113] (all to be multiplied by 10^{-6}). In a review of the field, Klemm[114,115] gave −20·1 × 10^{-6} as the most probable value for the susceptibility of the rubidium ion in solution. For the ion in crystals he gave −20·0 × 10^{-6} when the co-ordination number is 6 and −19·8 × 10^{-6} when it is 8; for the free ion he gave −21·5 × 10^{-6}. Another survey[116] recommends −22·5 × 10^{-6} but does not distinguish between the ion in solution and in crystals.[117] There are several useful reviews of methods for obtaining ionic susceptibilities and/or of the values resulting from them.[114,116,118–120]

Studies of the magnetic moments of ^{85}Rb and ^{87}Rb nuclei and of nuclear magnetic resonance have been made by a number of authors.[46,121–131] The best value for the magnetic moment of the ^{85}Rb nucleus has been given as 1·3522 ± 0·0004 nuclear magnetons and that of the ^{87}Rb nucleus as 2·7501 ±

0·005 nuclear magnetons.[132] Quadruple moments have also been discussed.[133-135]

As with other metals, the nuclear magnetic resonance frequency of rubidium in its compounds is lower than in the metal itself (Knight shift).[46,129] At room temperature the resonance shift $\Delta H/H$ has been measured as $0{\cdot}650 \times 10^{-2} \pm 0{\cdot}005 \times 10^{-2}$ for ^{85}Rb and $0{\cdot}653 \times 10^{-2} \pm 0{\cdot}002 \times 10^{-2}$ for ^{87}Rb with respect to an aqueous solution of rubidium hydroxide.[46] The resonance shift increases at the melting point and there is a peak in the resonance shift-temperature curve in the region of 254°K., but the total variation over a 150° range including the melting point amounts to no more than 3 to 4%.[130] Measurements of the magnetic resonance line width and its dependence on temperature have also been made.[46,130] Chemical shifts of the ^{87}Rb magnetic resonance have been found in the solid polycrystalline rubidium halides.[131]

The spins of ^{85}Rb and ^{87}Rb nuclei are $^5/_2$ and $^3/_2$ respectively.[122,123,136]

Electrode potentials

Chemical reaction of rubidium with water necessitates an indirect method for the determination of its standard electrode potential in aqueous solution (see Part I, page 404). From the e.m.f. measurements of Lewis and Argo[137] in 1915 on the cells:

Rb (solid) | RbI in ethylamine/ammonia | Rb (0·23% amalgam)
and Rb (0·23% amalgam | RbOH aq.; RbCl aq. | Calomel electrode

a value of –2·9242 V. at 25°C. is obtained[138] for the standard electrode potential of rubidium on the hydrogen scale. Here, and in all the values quoted below, the European convention is followed in denoting the sign of the electrode potential. In 1947, Bockris and Herringshaw[139] gave –2·98 V. as the best representative value for the standard potential after considering the above experimental value along with values calculated[140,141] from thermodynamic data. Using more recent thermodynamic data, Latimer[142] has calculated a value of –2·925 V. which agrees closely with Lewis and Argo's determination: –2·92 V. would now appear to be a better representative value for the standard potential in aqueous solution. Comparison with the other alkali metals is made on page 405 in Part I.

From measurements of the decomposition voltages of fused rubidium halides, a value of –2·744 V. has been arrived at for the rubidium potential at 18°C.[143]

Using spectroscopic and thermodynamic data, Gapon[144] has given +0·99 V. for the absolute electrode potential of rubidium.

Studies of the electrode potential of rubidium have been made in a number of non-aqueous solvents including liquid ammonia,[145,146] hydrazine,[147] formic acid,[148] formamide[149] and acetonitrile.[150] In comparing the potentials of elements in various solvents Pleskov[147,148] took the potential of the rubidium electrode in each solvent as an arbitrary zero since the free energy of solvation of the rubidium ion could be considered to be approximately the same in all solvents. Pleskov's values for the potentials of the other alkali metals relative to rubidium in each of the solvents ammonia, hydrazine, formic acid and water are given in Table XII on page 47 in Part I. A different basis of comparison allowing for differences in the free energy of solvation of rubidium in the various solvents has been given by Strehlow.[151]

Electromotive forces for the cell $Rb/RbCl/Cl_2$, where the rubidium chloride is in the solid or liquid state, have been calculated for temperatures between 25° and 1500°C. using thermodynamic data.[152] Similar calculations for other metals permit the construction of an electrochemical series for solid and fused chlorides.[152] The order of the metals varies slightly with temperature.

The rubidium ion was amongst the metal ions studied by Heyrovsky[153,154] in his first polarographic investigations; he found its deposition potential at a dropping mercury cathode in aqueous solution to be −1·796 V. relative to a normal calomel electrode. Discharge of rubidium ions can occur at a mercury cathode in neutral and alkaline solutions without the simultaneous discharge of hydrogen ions because of (*a*) compound formation between rubidium and mercury and (*b*) the high hydrogen overvoltage at mercury. The very negative potential does, however, limit the choice of supporting electrolyte; tetra-alkylammonium halides or hydroxides are virtually the only usable salts.[155] With tetramethylammonium chloride or hydroxide as supporting electrolyte, Heyrovsky[156,157] has given the half-wave potential of rubidium ions in aqueous solution as −2·07 V. relative to a normal calomel electrode. More recent studies[158,159] have given the half-wave potential in 0·1 M-tetramethylammonium hydroxide at 25°C. as 2·156 V. against a normal calomel electrode. Alcohol–water mixtures are frequently used in obtaining polarograms of the alkali metals since they give better developed waves than do purely aqueous media. In 50% ethyl alcohol, with 0·1 M-tetraethylammonium hydroxide as supporting electrolyte, the half-wave potential of rubidium is −1·99 V. relative to a saturated calomel electrode.[156] Rubidium has a half-wave potential so close to those of sodium (−2·07 V.), potassium (−2·10 V.) and caesium (−2·05 V.) (all in 50% ethyl alcohol + 0·1 M-tetraethylammonium hydroxide) that these four elements cannot be differentiated polarographically.[155]

In liquid ammonia, saturated with tetrabutylammonium iodide as supporting electrolyte, the half-wave potential of rubidium ions at −36°C. is −1·21 V. relative to a 0·1 N-$Pb/Pb(NO_3)_2$ reference electrode.[160]

Ionization potentials and electronegativity

Ionization potentials for rubidium have been arrived at by calculation from spectral series limits or by extrapolation along the isoelectronic sequences. Values, in electron volts, from two compilations of ionization potentials are shown in Table XIII; those in brackets have been obtained by the extrapolation method.

TABLE XIII.- IONIZATION POTENTIALS OF RUBIDIUM (ELECTRON VOLTS)

I	II	III	IV	V	VI	VII	VIII	IX	X	References
4·17	27·3	39·7	(53)	(71)	(86)	102	134	153	308	161
4·176	27·5	(40)	-	-	-	-	-	-	277	162

Rubidium may be ionized in various ways, e.g. by electron impact[163] or by the action of ultra-violet light (see page 2159). Ionization of rubidium also takes place on hot metal surfaces, for example those of tungsten and platinum, which have a work function less than the ionization potential of rubidium.[53,164-166] (See page 2148).

On Pauling's electronegativity scale rubidium has a value of 0·8 compared with values for the other alkali metals of Li, 1·0; Na, 0·9; K, 0·8; Cs, 0·7.[19]

Optical properties

From a study of the reflection of monochromatic plane polarised light from rubidium surfaces the values of Table XIV have been calculated for the refractive index (n), the extinction coefficient for normal incidence (K_0), the reflecting power for normal incidence (R), the principal angle of incidence ($\bar{\phi}$) and the principal azimuth ($\bar{\psi}$).[167]

Optical transmission curves for rubidium films of several thicknesses calculated from the data of Table XIV are shown in Fig. 3.[167]

TABLE XIV.- OPTICAL CONSTANTS OF RUBIDIUM

λ, (A.)	n	K_0	$R(\%)$	Φ	Ψ
5780	0·164	1·19	76·4	59° 38′	47° 36′
5461	0·157	1·05	74·2	57° 55′	47° 36′
4358	0·181	0·636	59·7	52° 1′	48° 16′
4047	0·275	0·373	37·6	47° 22′	49° 41′
3650	0·496	0·135	12·1	35° 37′	57° 33′
3341	0·745	0·090	2·39	37° 35·5′	80° 36′
3126	0·814	0·078	1·23	39° 39′	83° 17′
3022	0·833	0·071	0·98	40° 11·5′	84° 6′
2536	1·031	0·056	0·99	46° 0′	86° 48′

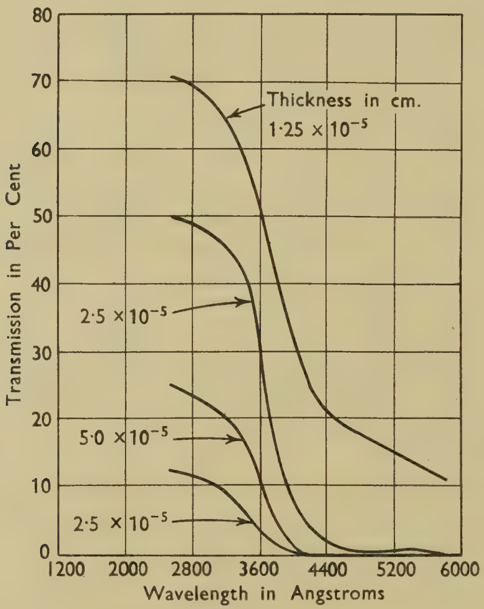

FIG. 3. OPTICAL TRANSMISSION CURVES FOR RUBIDIUM FILMS OF SEVERAL THICKNESSES

In the near ultra-violet region of the spectrum, thin films of rubidium that are quite opaque to visible light exhibit a high transparency.[167,168] Transmission starts to become appreciable at wave-lengths in the vicinity of 3,600 A.[168] Several theoretical treatments[168-175] have been concerned with the explanation of this transparency which is shown by all the alkali metals and extends to longer wave-lengths with increasing atomic number.

Anomalous dispersion has been studied in rubidium vapour in the vicinity of the first two doublets of the principal series.[176-178] Gabler[179] has studied magnetic double refraction (Voigt effect) in rubidium vapour.

Photoelectric properties

As is the case with the other alkali metals, the photoelectric properties of rubidium are dependent on the state of the surface and the film thickness, and are extremely sensitive to the presence of even slight traces of gas. For thick films of gas-free rubidium at −180°C. the photoelectric threshold has been given as 5900 A. which corresponds to a photoelectric work function of 2·1 e.V.[180] Partially outgassed samples have substantially lower values for the work function.[181] Values obtained for the work function in theoretical treatments have included 2·20[182] and 2·06 e.V.[183] A selective photoelectric maximum has been observed with rubidium at 4800 A.[184-185] Thoroughly outgassed surfaces in high vacuum show only a small selective effect and the yield at 4800 A. has been given as $3{\cdot}4 \times 10^{-4}$ coulombs per calorie.[3] The photoelectric sensitivity of thick rubidium films has been reported to vary reversibly and continuously with temperature between room temperature and −180°C.[186] At −180°C. the sensitivity to yellow light was about 25% lower than at room temperature while for blue light it was only 5% lower.

When rubidium is deposited on to gas-free silver by means of an atomic beam, the initial effect is that the threshold of the substrate is shifted to longer wave-lengths.[180] Brady[180] reported that at a thickness of 1·5 atomic layers the threshold reached an extreme position of 6200 A. and that at greater thicknesses it returned to the value (5900 A.) for the bulk metal. The photoelectric emission continued to increase up to a thickness of 5·0 atomic layers before dropping to that for bulk rubidium. There was no further change in the photoelectric properties for thicknesses greater than 12 atomic layers. The thickness values quoted are, however, probably too high because of the neglected roughness of the substrate.[187] Ives and Olpin[188] obtained, for rubidium films on a silver substrate, an extreme threshold of 7950 A. which coincided with the rubidium resonance line (7947 A.). The same relationship was found for the other alkali metals, but it has been considered[189] that their substrate probably contained oxygen which is known to cause large threshold shifts. Later work suggests that for surfaces completely free from contamination there would be no variation of photoelectric sensitivity with film thickness.[190] There are close similarities between the spectral response and the light absorption of thin rubidium films on a platinum-iridium mirror, both showing maxima at 3800 to 4000 A.[191]

The directional distribution of photoelectrons from rubidium surfaces irradiated by light incident at various angles and polarised in different planes has been studied.[192]

If a thin film of rubidium is separated from a metal substrate by a thin layer of a dielectric there is an increased photoelectric sensitivity. A silver substrate covered with approximately a monolayer of Rb_2O on which a thin film of rubidium is deposited has a threshold around 10,000 A. and shows selective maxima at ~4100 A. and ~6600 A.[193-195] In the ultra-violet at wavelengths below 3000 A. the spectral response of the photoelectric emission exhibits several narrow peaks which are related to the absorption spectrum of the oxide.[196]

Still higher sensitivities can be achieved by the use of more complicated photo-cathodes. For example, a composite surface $Rb{-}Ag{-}Rb_2O{-}Ag$ has two selective maxima, one between 3300 A. and 3700 A., and one at about 5500 A., and for light from a gas-filled tungsten lamp (colour temperature, 2700°K.) it yields 10 to 15 μamps. per lumen.[197,198]

Monatomic films of rubidium deposited spontaneously on cold glass surfaces in an evacuated vessel containing rubidium have been reported to show a smaller ratio of selective to normal photo-electric effects than films deposited on conducting surfaces.[199,200] These films on glass exhibit ohmic resistance in the dark, and the resistance decreases on exposure to light.[200]

Photoionization.

Photoionization of rubidium vapour has been studied by space charge methods at wave-lengths of 2350–3050 A.[201] and 2150–3700 A.[202] The photo-

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sensitivity is a maximum at the wave-length of the limit of the principal spectral series (2968 A.) where the atomic absorption cross section is $1\cdot1 \pm 0\cdot2 \times 10^{-19}$ cm.^{2}.[201] By 2350 A. it has dropped to about 5% of its value at the series limit.[201] Lawrence and Edlefsen[202] found the variation of the ionization per unit of light intensity, β_ν, with frequency, ν, on the higher frequency side of the maximum to be represented approximately by the equation

$$\beta_\nu = \text{constant}/\nu^3\ (\nu - \nu_0)$$

where ν_0 is the series limit frequency. Theoretical treatments are capable of reproducing the main features of the experimental results.[203,204] Photoionization can also occur at wave-lengths greater than that of the spectral series limit (which is the wave-length corresponding to the ionization potential).[201,202]

Radioactivity

Rubidium exhibits a natural radioactivity as discovered by Thomson[205] in 1905. The seat of the radioactivity is the ^{87}Rb isotope[206-208] which is present in natural rubidium to the extent of approximately 28% (see page 2170) and undergoes a simple beta-decay.[209,210]

$$^{87}\text{Rb} \longrightarrow {}^{87}\text{Sr} + \beta^-$$

That the radioactivity is due to ^{87}Rb and not, as had been suggested earlier,[211,212] to a rare isotope ^{86}Rb was shown conclusively by Hahn *et. al.*,[206] who found the strontium from an old mineral rich in rubidium to consist of over 99% ^{87}Sr with only a few tenths of a percent of the normal ^{88}Sr, and by Hemmendinger and Smythe,[208] who carried out a small-scale separation of the rubidium isotopes with the aid of the mass spectrograph. The ^{87}Rb separated in the latter work was shown to be radioactive and there was no other isotope with an appreciable activity compared with it. A number of determinations of the half-life of this isotope have given values in the vicinity of 6×10^{10} years.[209,210,213-218] The ^{87}Sr/^{87}Rb ratio can be used as a measure of the geological age of minerals.[219,220] Rubidium has a higher β-ray activity[221-223] than potassium but the radiation has a lower penetrating power.[224-227]

Miscellaneous physical properties

Ultrasonic waves of frequency 12 Mc./sec. have a velocity of 1260 ± 10 m./sec. in liquid rubidium at its melting point.[37] Between the melting point and 160°C. the temperature coefficient is $-0\cdot4$ m./sec./degree.

The coefficient of diffusion of rubidium in mercury at 8 to 15°C., as calculated from atomic radius and viscosity data with the aid of the Stokes-Einstein equation, is $0\cdot44$ cm.^{2} per 24 hr.[228] There is reasonable agreement with the older experimental value of $0\cdot46$ cm.^{2} per 24 hr. at $7\cdot3$°C. (Mellor, II. 456)

Justi[76] obtained $-0\cdot0018$ for the Hall constant of rubidium at room temperature and $-0\cdot0091$ at 90°K. Values determined by other workers have been considerably higher. Krautz[229] obtained $-0\cdot00592 \pm 0\cdot00014$ for the room temperature value. whilst Fakidov[230] obtained $-0\cdot005$ for solid rubidium and $-0\cdot0042 \pm 0\cdot0005$ for the liquid. Theoretically calculated values for the Hall constant are $-0\cdot00579$[229] and $-0\cdot0058$.[231]

A value of $1\cdot0056$ has been obtained for the dielectric constant of rubidium vapour at 500°C. and a pressure of $0\cdot6$ mm.Hg.[232]

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PROPERTIES OF THE RUBIDIUM ION

Some properties of the rubidium ion, and some that relate to both the metal and its ion, have been dealt with under the appropriate sections above. Other properties of the Rb^+ ion will be considered here.

The Ion in Solution.

The heat and free energy of formation of the aqueous rubidium ion at 25°C. are −58•9 and −67•45 kg.-cal.g.-ion^{-1} respectively.[1] From thermal data for the two reactions $RbClO_3$ (solid) → Rb^+ (aq.) + ClO_3^- (aq.) and $RbClO_4$ (solid) → Rb^+ (aq.) + ClO_4^- (aq.) a mean value of 28•7 ± 0•7 g.-cal.-g.-ion^{-1} degree^{-1} has been derived for the entropy of the rubidium ion (relative to that of the hydrogen ion) in aqueous solution at 25°C.: values from the individual reactions were 28•9 ± 0•8 and 28•5 ± 1•0 respectively.[2] The U.S. Bureau of Standards selected value[1] for the entropy of the aqueous rubidium ion at 25°C. is 29•7 g.-cal.g.-ion^{-1}degree^{-1}.

After calculating the effective diameter of the hydrated rubidium ion by a variety of methods, Kielland[3] took a rounded value of $2{\cdot}5 \times 10^{-8}$ cm. for this dimension and then used the Debye–Hückel theory to compute activity coefficients of the rubidium ion in aqueous solution at 25°C. The resulting values are shown in Table XV.

TABLE XV.- ACTIVITY COEFFICIENTS OF THE Rb^+ ION IN AQUEOUS SOLUTION AT 25°C.

Total Ionic Concentration	Activity Coefficient
0•001	0•975
0•002	0•964
0•005	0•945
0•01	0•924
0•02	0•898
0•05	0•85
0•1	0•80
0•2	0•75

Methods considered by Bockris (see Part I, page 56) to give a measure of primary solvation have led to values of two (from ionic entropy) and zero (from partial molar volume) for the hydration number of the rubidium ion.[4] Higher values result from transference, dialysis and other methods.[5,6]

Values calculated for the heat of hydration of the Rb^+ ion have included 69,[7] 69•2,[8] 74[9] and 87[10] kg.-cal./g.-ion, while the free energy of hydration has been calculated as 66•5,[7] 67•5,[8] and 76•9[11] kg.-cal./g.-ion. The entropy of hydration has been given as 6[8] and 8•8[7] g.-cal./degree/mole.

A recent compilation,[12] using conductivity and transport number data from several sources, gives the values in Table XVI for the equivalent conductivity or mobility of the rubidium ion at infinite dilution in water.

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TABLE XVI.- MOBILITY OF THE Rb^+ ION AT INFINITE DILUTION IN WATER

Temp., °C.	λ_∞
0	43·9
5	$50{\cdot}1_3$
15	$63{\cdot}4_4$
18	66·5
25	$77{\cdot}8_1$
35	$92{\cdot}9_1$
45	$108{\cdot}5_5$
55	$124{\cdot}2_5$

At 0° and 18°C. the values are said to be reliable to within two or three units in the first decimal place, while those at the other temperatures are reliable to within one unit in the first decimal place. Mobilities of the rubidium ion in a number of non-aqueous solvents have been estimated from conductivity data for rubidium salts.[13,14]

Nernst's limiting diffusion formula $D^\circ = RT\ \lambda_\infty/zF^2$ may be used in conjunction with the above mobility data to yield values for the diffusion coefficient, D°, of the Rb^+ ion at infinite dilution. At 25°C. a value of $2{\cdot}07 \times 10^{-5}$ $cm.^2 sec.^{-1}$ is obtained in this way for the self-diffusion coefficient of the rubidium ion at infinite dilution in water. By the use of an open-ended capillary tube method and employing ^{86}Rb as radio-tracer the values in Table XVII have been determined for the self-diffusion coefficient of the rubidium ion in aqueous solutions of rubidium iodide at 25°C.[15]

TABLE XVII.- SELF-DIFFUSION COEFFICIENTS OF Rb^+ IN RbI (aq.) AT 25°C.

Rb^+ Concn. g.-ion/litre	$D \times 10^5$ $cm.^2/sec.$
0·010	2·055 ± 0·025
0·038	2·047 ± 0·010
0·070	2·037 ± 0·020
0·110	2·017 ± 0·010
0·185	2·008 ± 0·015
0·370	2·004 ± 0·010
0·640	1·995 ± 0·010
0·927	1·993 ± 0·010

A value of 0·0056 has been calculated for the specific viscosity of the rubidium ion in 0·1 N. aqueous solution.[16]

Magnetorotary powers, $[M]$, of the rubidium ion (in min. $cm.^2$ $gauss^{-1}$ $g.\text{-}ion^{-1}$) derived from the work of Okazaki on the Faraday effect in aqueous salt solutions are as follows, a value of zero being assumed for the hydrogen ion.[17]

Wave-length, A.	5900	5500	5100	4700	4300	3900	3500
$[M]$	0·44	0·46	0·53	0·65	0·84	1·05	1·23

Refs. p. 2168

Okazaki's molecular magnetorotation constant, Φ (see Part I, page 422) has a value of $1{\cdot}51 \times 10^{-14}$ for the rubidium ion.

The refractivity of the rubidium ion in aqueous solution for the sodium *D*-line is 3·58.[19]

Exchange between Rb^+ ions and other ions has been studied with synthetic cationic exchange resins[20-24] as well as with natural exchangers such as minerals.[27-31] (See also page 1542).

The Gaseous Ion.

The most widely used method of producing gaseous rubidium ions consists of heating a rubidium compound, mixed with other substances, on a metal filament.[32-43] Mixtures of iron oxide with about 1% of a rubidium compound and, in some cases, with about 1% of aluminium oxide – *i.e.* Kunsman catalysts[32-38] – have found extensive application as have glass melts of silica, alumina and rubidium oxide.[39-41] The ions may be accelerated to the required potential in an electric field. Rubidium ions may also be produced by photoionization (see page 2159) or by surface ionization on a suitable metal such as tungsten (see page 2157).

The heat of formation of the gaseous rubidium ion is 118·297 kg.-cal. g.-ion^{-1} at 298·16° K.[1]

In various gases at one atmosphere and 20° C., the mobility of the Rb^+ ion (in cm./sec./volt/cm.) is as follows:[36,44]

Helium	20·9	Xenon	1·12
Neon	7·08	Hydrogen	13·4
Argon	2·37	Nitrogen	2·39
Krypton	1·61		

Later measurements in the rare gases are in close agreement with these.[40] The temperature variation of the mobility in krypton has been determined over the range 90–455° K.; at the higher temperatures the mobility at constant density appears to reach a constant value.[41] Alkali metal ions, in the presence of water vapour, acquire a cluster of water molecules which reduces their mobility. The mobility of the Rb^+ ion has been studied in helium, neon, argon, krypton and xenon all containing small concentrations of water vapour, and the water vapour has been found to have the greatest effect in helium, where it reduces the mobility by 40%.[40] Other measurements have been made in pure water vapour.[45] The mobility of Rb^+ ions in a bunsen flame has also been measured.[46]

Several studies have been made of the ionization of the inert gases by rubidium and other alkali metal ions.[47-54,37,38] Beeck and Mouzon,[50-52] who measured the potentials (ion velocities) required by rubidium ions to ionize neon, argon, krypton and xenon to be 420 V., 180 V., 100 V., and 145 V. respectively, found that, in general, an inert gas is most easily ionized by the alkali ion with an atomic number nearest its own. It has, however, been suggested[38] that there was some interference from secondary electrons in these measurements. By the use of a space-charge method sensitive to any resulting positive ions but unaffected by secondary electrons from the walls, values of 135 V., 97·5 V., and 150 V., have been obtained for the potentials required for ionization of argon, krypton and xenon respectively.[38]

Optical excitation by rubidium ions has been studied in the rare gases[42] and in mercury vapour.[55]

Reflection of ions and the emission of secondary electrons has been studied on bombarding metal surfaces with rubidium ions.[56-58]

The refractivity of the free rubidium ion for the sodium *D*-line is 3·58.[19] Values for the polarisability of the rubidium ion include $1{\cdot}42 \times 10^{-24}$,[59] $1{\cdot}485 \times 10^{-24}$,[19] $1{\cdot}5 \times 10^{-24}$,[60] and $1{\cdot}81 \times 10^{-24}$.[61] Other dielectric parameters of the rubidium ion have been evaluated.[62-64]

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SOLUTIONS OF RUBIDIUM

Like the other alkali metals, rubidium dissolves readily in liquid ammonia to give deeply coloured solutions. The rate of solution is greater than for the alkali metals of lower atomic weight,[1] and the heat of solution is zero.[2] Rubidium solutions are less stable than those of lithium, sodium and potassium; amide formation occurs with the accompaniment of hydrogen evolution[3-5] (see page 2172).

$$Rb + NH_3 \rightarrow RbNH_2 + \tfrac{1}{2}H_2$$

Decomposition of the solutions is catalysed by even minute traces of impurities. (cf. Part I, page 427).

The same coloration and absorption is shown by rubidium adsorbed on films of solid ammonia at −183°C. and a pressure of 10^{-3} to 10^{-4} mm.Hg as by solutions of rubidium in ammonia.[6] Optical absorption starts at about 5600 A. and increases towards longer wave-lengths.[6]

Rubidium is also freely soluble in methylamine.[7]

Searches for a solvent for a rubidium salt that is not also a solvent for the metal have been made in connection with the determination of the electrode potential of rubidium.[7] Lewis and Argo[7] found rubidium to be only slightly soluble in an ammonia/ethylamine mixture containing 7·9 mol.-% of ammonia. With increasing ammonia content the solubility of rubidium increased, but at 13·4 mol.-% of ammonia a second layer of metallic appearance was formed. Whilst pentane and liquid ammonia are miscible in all proportions, addition of a small amount of rubidium to such a mixture causes separation into two phases, the rubidium dissolving only in the phase consisting chiefly of ammonia.[7]

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ATOMIC WEIGHT AND ISOTOPES

Up to 1937 the internationally accepted value for the atomic weight of rubidium was 85·44 based on the work of Archibald[1] in 1904. In 1937[2] it was changed to its present[3] value of 85·48 following redeterminations of the RbCl: Ag, RbBr:Ag, and RbBr:AgBr ratios by Archibald and co-workers.[4,5]

For determining the RbCl:Ag ratio,[4] the rubidium salt was purified by fractional crystallization first as the dichloroiodide (10 times), then as the acid tartrate (5 times), and finally as the chloride (3 times). Rubidium chloride was prepared for weighing by fusion under nitrogen and was compared with pure silver by the standard solution method of Johnson[6] (see page 1553). The resulting value for the atomic weight was 85·482. Rubidium bromide was obtained from the rubidium nitrate formed during the chloride analyses.[5] There was an intermediate recrystallisation as the acid tartrate, and the bromide was further recrystallised. Nephelometric determination of the RbBr:Ag ratio gave Rb = 85·483 whilst gravimetric estimation of the RbBr:AgBr ratio gave Rb = 85·478. There is good agreement between the three ratios which yield an average atomic weight of 85·481.

There are two natural rubidium isotopes with mass numbers 85 and 87. Several mass spectrographic determinations of their relative abundance are in fair agreement yielding ^{85}Rb/^{87}Rb ratios in the vicinity of 2·6 (Table XVIII). In a review of abundance ratio data, Bainbridge and Nier[15] in 1951 chose 2·591 ± 0·003 as the best value for the ^{85}Rb/^{87}Rb ratio. This corresponds to 72·15 ± 0·03 atom-% ^{85}Rb and 27·85 ± 0·03 atom-% ^{87}Rb.

TABLE XVIII.- NATURAL RELATIVE ABUNDANCE OF ^{85}Rb AND ^{87}Rb

Year	Authors	^{85}Rb/^{87}Rb	% ^{85}Rb	% ^{87}Rb	Ref.
1932	Aston	3·0	75	25	7
1934	Brewer & Kueck	2·59 ± 0·04	72·1	27·9	8
1935	Bondy *et al.*	2·68	72·8	27·2	9
1936	Brewer	2·59 ± 0·01	72·1	27·9	10
1936	Nier	2·68 ± 0·02	72·8	27·2	11
1938	Brewer	2·60 ± 0·01	72·2	27·8	12
1947	Paul	2·64 ± 0·03	72·5	27·5	13
1950	Nier	2·591 ± 0·003	72·15	27·85	14

An ^{85}Rb/^{87}Rb abundance ratio of 2·591 taken in conjunction with the masses of these two isotopes (see below) also leads to an atomic weight of 85·48.

Brewer and Baudisch[16] reported a normal ^{85}Rb/^{87}Rb ratio in old mineral formations of marine plant origin and their associated mineral waters in which some fractionation of the potassium isotopes was found (see page 1555). Brewer[12] obtained 2·61 ± 0·01 for the ^{85}Rb/^{87}Rb ratio in lepidolite and zinnwaldite minerals, in rubber seed and in apple seed, whilst in artificial spodumene he obtained the slightly lower value of 2·59 ± 0·01. Rubidium ion sources show no isotope effect of free evaporation similar to that found with lithium[10] (cf. Part I, page 65).

Nier,[11] who made a mass spectrographic search for other naturally occurring rubidium isotopes, set the upper limits for their abundance relative to ^{85}Rb as:

^{80}Rb, ^{81}Rb, ^{82}Rb, ^{89}Rb and ^{90}Rb	1:100,000
^{83}Rb	1:60,000
^{84}Rb	1:12,000
^{86}Rb	1:13,000
^{88}Rb	1:22,000

A number of rubidium isotopes with short half lives have been produced artificially by nuclear reactions. A review, which also summarises methods of production and disintegration schemes, lists the following:[17] (see also pages 2454 and 2455

Isotope	Approx. Half Life	Isotope	Approx. Half Life
^{81}Rb	4·7 hr.	^{90}Rb	2·7 min.
^{82}Rb	6·3 hr.	^{91}Rb	14 min.

Isotope	Approx. Half Life	Isotope	Approx. Half Life
^{83}Rb	100 days	^{92}Rb	1·3 min.
^{84}Rb	36 days	^{93}Rb	-
^{86}Rb	19·5 days	^{94}Rb	-
^{88}Rb	18 min.	^{95}Rb	-
^{89}Rb	15 min.	^{97}Rb	-

There are also metastable excited states of some of these.

Mass spectrometer measurements of mass doublets containing rubidium have given the masses of the ^{85}Rb and ^{87}Rb isotopes as 84·93920 ± 0·00008 and 86·93709 ± 0·00017 respectively:[18] ^{1}H = 1·008146 ± 0·000005 and ^{12}C = 12·003842 ± 0·000004 were taken as standards in these measurements (cf. page 1556). Measurements[19] with a magnetic time-of-flight spectrometer have given ^{85}Rb = 84·931 ± 0·0015 and ^{87}Rb = 86·9295 ± 0·0020.

Hemmendinger and Smythe[20] separated the two rubidium isotopes with the aid of the mass spectrograph and showed ^{87}Rb to be responsible for the natural radioactivity of rubidium (cf. page 2160). Rubidium is among elements whose isotopes have been successfully enriched using production-scale mass spectrographs originally developed to enrich uranium–235.[21]

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SECTION LXV

THE CHEMICAL REACTIONS AND ALLOYS OF RUBIDIUM

By (Mrs.) F. DICKINSON

CHEMICAL REACTIONS

Rubidium forms four oxides: Rb_2O, yellow cubes; Rb_2O_2, yellow cubes; Rb_2O_3, a black powder; and RbO_2 a yellow powder.[1]

The monoxide is obtained when dry oxygen is passed over excess of rubidium contained in a previously evacuated vessel. When oxidation is complete the apparatus is again evacuated and the reaction mass heated to 160–180°C. so that excess metal can distil over leaving behind the pure crystalline monoxide. On heating to 400°C. it decomposes to rubidium peroxide, Rb_2O_2, and rubidium which is volatilised. The final thermal decomposition product of the peroxide is rubidium monoxide.[2] Brewer and Mastick[3] have shown by theoretical calculations that the monoxide is unstable at 1000°K. and dissociates.

Rubidium, contained in an aluminium boat in an evacuated glass tube, may be converted to the peroxide by allowing it to absorb the calculated amount of oxygen and then melting the mixture. On cooling, the brown liquid solidifies to yellow crystals of the peroxide. The peroxide is also formed by the rapid oxidation of rubidium in liquid ammonia at −50°C. in the presence of a trace of rubidium amide, but the product is not pure. Incomplete dissociation of the superoxide, RbO_2, gives rubidium peroxide with some monoxide.[2]

The end product of the oxidation of rubidium with oxygen is rubidium superoxide: the metal is heated just below its m.p. in oxygen at atmospheric pressure until absorption is complete. When oxygen is slowly led over rubidium, freshly prepared by the reduction of pure rubidium sulphate, the metal ignites and a vigorous reaction occurs producing the superoxide. This oxide is also formed by the oxidation of rubidium or rubidium peroxide in liquid ammonia; after long stirring reddish yellow crystals are deposited.[2]

The spontaneous oxidation of rubidium amalgam exposed to air is described by Rinck and Chassain.[4] The reaction is complete in 4 to 7 days and analysis of the oxidised surface layer on the amalgam shows the formation of $Rb_2O_{2.9}$ to $Rb_2O_{3.5}$ approaching Rb_2O_4. The variation in composition is probably due to the great reactivity of the amalgam with moisture. The oxide oxidises some of the mercury to mercurous oxide, the amount of which increases with time of contact but is not in stoicheiometric relationship with that of the rubidium oxide furnishing the oxygen. On treatment with water the oxidised amalgam gives a vigorous evolution of oxygen leaving a green powder, similar to that obtained with oxidised potassium amalgam, and believed to be Hg_2O. The so-called tetroxide of rubidium has been shown by Helms and Klemm[5] to contain the O_2^- ion and its formula is RbO_2 and not Rb_2O_4.

When oxygen is passed over rubidium contained in an evacuated vessel until absorption is complete and the mixture is heated to the melting point, rubidium combines with the amount of oxygen required to form the trioxide.

It is also formed when the superoxide, RbO_2, is heated at 550°C. at low pressures. At 600°C. the black trioxide decomposes to the monoxide with evolution of oxygen.[1,2]

When ozone is led into a liquid ammonia solution of rubidium a compound apparently analogous to that formed by the action of ozone on solid potassium hydroxide is obtained. The compound cannot however be isolated in the dry state free from ammonia:[6] it is thought to be $RbOH.O$ or $(RbOH)_2O_2$.

When pure dry hydrogen is passed over pure rubidium contained in an iron boat in a glass tube heated to about 300°C., crystals of rubidium hydride are formed in the cooler part of the tube. Hydrogenation at 300°C.–400°C. is very slow and a static method may be used in a vacuum-tight apparatus, the rubidium being contained in a nickel boat. Rubidium, prepared from rubidium carbonate and magnesium powder, is distilled and cooled and then slowly vaporised in a stream of hydrogen at one atmosphere pressure at 300°C.–400°C. The hydrogenation is not complete if the metal is vaporised quickly.[2,7] Rubidium deuteride, RbD, has been prepared in an analogous manner.[2,8]

A blue light is observed on the surface of rubidium when it is heated to give a vapour pressure of about 0·1 mm. in a long tube through which moist hydrogen at a pressure of about 0·1 to 0·05 mm. is streamed while a powerful electric discharge is passed. A possible explanation of spectrum excitation by atomic hydrogen is that a three-body collision of two hydrogen atoms and a metal atom takes place in which part of the energy of recombination is expended in producing excitation of the metal atom.[9,10] The mechanism of reactions involving excited electronic states, *i.e.* reactions of the alkali metals with hydrogen in which chemiluminescent and quenching reactions occur, is discussed by Magee and Taikei.[11]

The dissociation pressures of rubidium hydride given in Table I have been measured by Herold.[12]

TABLE I.- DISSOCIATION PRESSURES OF RUBIDIUM HYDRIDE

Temp. °C.	p mm. Hg
350	476
308·5	109
289	49·6
266·5	18·2
246	7·1

The equation given for the above range of temperatures is: $\log p = -5680/T + 11{\cdot}80$. The calculated heat of formation of rubidium hydride is 12·980 kg.-cal. per g.-mole ± 1·5%.

Rubidium dissolves in water to form rubidium hydroxide. The heat of formation, Rb (solid) + H_2O (solid) = RbOH (solid) + 0·5 H_2, is 31·56 kg.-cal.[2]

Fischer and Schröter[13] have investigated the effect of passing an electric discharge through nitrogen using the alkali metals as electrodes; the products are rapidly chilled to prevent decomposition. It is said that nitrides of sodium, potassium and rubidium are formed. The compounds formed when the discharge is passed through a liquid mixture of 90% of argon and 10% of nitrogen are black in colour and contain fine metallic dust. With acids these nitrides form ammonia, not hydrazine salts. Moldenhauer and Mottig[14] find that when nitrogen activated by an electric discharge reacts with rubidium, the azide is formed together with a small amount of nitride which is formed apparently from the azide. According to Wattenburg[15] the stability of rubidium nitride is so slight that only the azide is obtained by the action of active nitrogen.

The alkali metals react with either liquid or gaseous ammonia to form amides. With liquid ammonia the times of reaction under comparable condi-

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tions are: Cs, 15 min., Rb, 30 min., K, 60 min., and Na and Li several days; *i.e.* the heavier the metal the more easily it reacts. The amides are white crystalline solids. The heat of formation of rubidium amide is 27 kg.-cal. per g.-mole.[16,17]

Liquid ammonia solutions of rubidium are dark blue, much less dense than liquid ammonia, conduct the electric current and show strong paramagnetism. On standing, rubidium reacts with liquid ammonia slowly liberating hydrogen and forming the amide; the reaction is accelerated by heat, by short ultraviolet light and by catalysts such as platinum, iron or asbestos.[18,19] Rubidium is soluble in methylamine and the solution is blue as with liquid ammonia.[19]

Rubidium burns in chlorine, bromine and iodine vapours. The heat of formation of rubidium fluoride: Rb (solid) + 0·5 F_2 (gas) → RbF (solid) is $\Delta H_{298} = -131{\cdot}28$ kg.-cal.;[20] other values given are −132·8 kg.-cal.[21] and −107·85 to −107·95 kg.-cal. at about 288°K.[2] The total energy change for the formation of the fluoride from its elements is given as 225 kg.-cal.[22] The relationship between the heat of formation, lattice energy and properties of the ion has been discussed by Grimm.[23]

For the reaction Rb (solid) + 0·5 Cl_2 (*g*) → RbCl (solid), $\Delta H_{298} = -102{\cdot}9$ kg.-cal.,[20] $\Delta H_{288} = 105{\cdot}00$ kg.-cal.[2] The total energy change in the formation of the chloride from its elements is 238 kg.-cal.[22] The relationship between the heat of formation, lattice energy and properties of the ion has also been discussed by Grimm.[23]

The heat of formation of rubidium bromide: Rb (solid) + 0·5 Br_2 (gas) → RbBr (solid) at about 15°C. is −99·21 kg.-cal. and for rubidium iodide under the same conditions −87·45 kg.-cal.[2] The total energy changes for the formation of the bromide and iodide from their elements are respectively 239 and 243 kg.-cal.[22] The dependence of the volume of the components of the halides on the heats of formation is discussed by Schutz and Ephraim[24] and the relationship between the heat of formation, the lattice energy and the ion properties by Grimm.[23]

A chemiluminescence is observed at 2000–9000 A. when iodine and rubidium vapours react at low pressures, not exceeding 15 mm. The first lines of the principal series and the second lines of rubidium as well as faint apparently continuous bands are seen.[25]

In his collection of data of elements which exhibit anomalous valencies, Klemm lists the following compounds: $Rb^{I}[Rb^{V}F_6]$; $Rb^{I}[Sb^{V}F_6]$; $RbSbF_6$,-$6RbF_3$.[26]

Rubidium burns in sulphur to form rubidium sulphide. The monosulphide, Rb_2S, is formed together with some polysulphides when sulphur vapour is passed over molten rubidium at 200°–300°C.[2] To prevent the formation of polysulphides, mercury sulphide may be substituted for sulphur and when the reaction is complete, mercury and excess rubidium are distilled off at 250°C.[27]

The heat of formation for the reaction: 2Rb (solid) + S (solid) → Rb_2S (solid) is −83·2 kg.-cal.;[20] −87·1 kg.-cal.[2]

Thermal analyses of the system rubidium–sulphur in the region of Rb_2S_2 to $Rb_2S_{6\cdot8}$ indicate the existence of Rb_2S_2 m.p. about 420°C.; Rb_2S_3 m.p. about 213°C.; Rb_2S_4 m.p. above 160°C.; Rb_2S_5 m.p. 231°C. and Rb_2S_6 m.p. 201°C. Desulphurisation of the pentasulphide by heating in hydrogen begins slowly at the b.p. of sulphur, increases above 500°C. and at 810°C. the disulphide is formed. This compound volatilises at about 950°C. and solidifies in the cold end of the tube to a pale orange-red incrustation. Desulphurisation in nitrogen produces the trisulphide which is volatile at 900° to 1000°C.[2]

The sulphides are also prepared from the elements in liquid ammonia.[28] The monosulphide is white, the disulphide yellow, the trisulphide red, the tetrasulphide reddish brown and the pentasulphide brown. (See also page 2178).

Pearson and Robinson[29] have shown that molten rubidium in toluene reacts with sulphur to form rubidium tetrasulphide, Rb_2S_4; under similar conditions lithium gives the monosulphide, sodium the trisulphide and potassium, like rubidium, the tetrasulphide. When rubidium is dissolved in absolute alcohol and the solution saturated with hydrogen sulphide, excess of the gas being removed by boiling in a stream of nitrogen, rubidium hydrogen sulphide is obtained. Reaction of this compound in absolute alcohol with various amounts of sulphur results in the formation of higher sulphides in solution, either tetra- or penta- and, by analogy with potassium, most probably the pentasulphide. The most stable sulphides are the di- and pentasulphides, Rb_2S_2 and Rb_2S_5 and the highest stable sulphide obtained by melting rubidium with sulphur is the hexasulphide, Rb_2S_6.

Rubidium selenide, Rb_2Se, is formed when selenium is distilled on to rubidium. On heating in vacuum at about 650°C. there is a slight separation of metal; rubidium vapour is not taken up again at either ordinary or higher temperatures.[2,27] (See also page 2178). The selenide is also formed when selenium is replaced by mercury selenide, excess metal and mercury being distilled off at 250°C.[27,28]

Rubidium telluride, Rb_2Te, is formed by the action of tellurium on rubidium at high temperatures. Near its melting point a certain amount of evaporation occurs without decomposition. Heating at about 690°C. in a vacuum results in separation of some metal; rubidium vapour is not taken up again at ordinary or at higher temperatures.[2,27] The telluride is also formed when excess rubidium is heated with mercury telluride and excess rubidium and mercury are distilled off at 250°C.[27,28] (See also page 2178).

The above reactions must be carried out in the absence of air and moisture in an evacuated apparatus. Rubidium hydroselenide and hydrotelluride are prepared by treating rubidium alcoholate with hydrogen selenide or hydrogen telluride in the absence of air and moisture. Crystalline compounds are obtained by distilling off the alcohol in a vacuum.[30]

Rubidium like potassium reacts with carbon in the form of graphite, soot or active charcoal, which swell up as they become permeated with the molten metal, disintegrate and give out heat. Details of the experiments carried out by Fredenhagen and Cadenbach are shown in Table II.

TABLE II.- REACTION OF RUBIDIUM WITH CARBON

Temp. °C.		Pressure mm. Hg	Adsorbent	Amount of Rubidium per mole of C
C	Rb			
450	300	1·2	Graphite	0·12
450	300	1·2	Soot	0·12

The product RbC_8 is pyrophoric and dark copper-red in colour. Because of the relatively higher vapour pressure of rubidium the reaction can be carried out at a lower temperature than with potassium, with the result that the glass container is not markedly attacked.[31] According to Schleede and Wellmann[32] the above compound has a similar layer lattice to that of the potassium compound KC_8, having metal planes alternating with the basal planes of graphite. By heating the brown compound at a higher temperature a black compound is formed in which every two graphite planes are followed by a metal plane, the composition being represented by the formula RbC_{16}. According to Rüdorff and Schulze[33] thermal decomposition of RbC_8 gives in turn RbC_{24}, RbC_{36}, RbC_{48} and RbC_{60} all of which are heterogeneous in crystal structure and weakly paramagnetic. The equilibria: $3C_8M \rightleftharpoons C_{24}M + 2M$,

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where M is potassium, rubidium or caesium and C refers to graphite, have been studied by Herold[34] by passing the metal vapour over graphite at various temperatures up to 600°C. A series of insertion compounds is formed. The heat of formation Q when one atom of metal is fixed *i.e.* $C_{24}M + 2M$ (vapour) $\rightarrow 3C_8M + 2Q$ is 3·4, 5·85 and 10·1 kg.-cal. where M = K, Rb or Cs respectively, with all in the liquid phase.

Glass and porcelain are attacked by molten rubidium; Pyrex glass is attacked at a higher temperature than ordinary glass and Suprax glass is even more resistant than Pyrex.[2]

Rubidium reacts with a solution of anhydrous hydrogen cyanide in benzene to form rubidium cyanide.[2]

Acetylene is decomposed even on slightly warming with rubidium with voluminous separation of carbon. The acetylide, $RbHC_2$, is formed when acetylene is led into a solution of rubidium in liquid ammonia. The transparent crystals float on carbon tetrachloride but sink in ether and melt with decomposition below 300°C. On heating in a vacuum at 300°C. the compound is converted to rubidium carbide, Rb_2C_2.[2]

When excess of rubidium is treated in an evacuated vessel with phosphorus, a black product is formed which on heating in a vacuum at about 450°C. gives rubidium phosphide, Rb_2P_5. This compound is yellow at room temperature and on warming becomes reddish brown. It melts at about 650°C. with decomposition; when heated in hydrogen at 300°C. phosphorus is split off and a black phosphide obtained. Transparent crystals are obtained when a liquid ammonia solution of the phosphide (yellow) is concentrated at −18°C. The crystals effloresce at room temperature and lose ammonia to give amorphous pentaphosphide.[2]

Rubidium reacts violently with vanadium oxytrichloride $VOCl_3$, at 60°C.[35]

Thermal analysis of the rubidium–mercury system indicates the presence of the following compounds: Rb_3Hg_4, $RbHg_2$, Rb_2Hg_7, Rb_5Hg_{18}, Rb_2Hg_9, $RbHg_6$, $RbHg_9$ and Rb_7Hg_8. (See also page 2182).

Rubidium dispersions, stable against settling and agglomeration and in which the dispersed metal does not exceed 50μ in size, are prepared from an emulsion of finely divided molten particles of the alkali metal in an inert liquid hydrocarbon of b.p. higher than the m.p. of rubidium in the presence of an emulsifying agent. The emulsifying agents suggested are (1) alkali metal alkoxides, MOR, where M is the alkali metal and R an aliphatic, *cyclo*aliphatic or aromatic radical and (2) an alkali metal organic compound *i.e.* compounds having at least one residue of the structure C:CCM where M is the alkali metal.[36]

Rubidium is displaced from its hydroxide by heating with iron at a pressure of 0·001 mm. at 500°C. to 700°C. The reaction takes place according to the equation: $3RbOH + 2Fe \rightarrow Fe_2O_3 + 3Rb + 1{\cdot}5H_2$. The yield of metal is about 50%, probably because a non-reducible ferrite is formed in the course of the reaction.

When rubidium sulphate is heated in an evacuated apparatus with iron, reaction begins at 800°C. and is rapid at 1000°C. After heating for one hour at 1100°C. an 80% yield of rubidium is obtained: $2Rb_2SO_4 + 3Fe \rightarrow Fe_2O_3 + FeS + SO_2 + 1{\cdot}5O_2 + 4Rb$.[37]

Accounts of the chemical properties of the alkali metals, including rubidium, have been given up to about 1936 by Guillet,[38] up to 1940 by Klemm[30] and up to about 1948 by Sidgwick.[39]

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Reactions of rubidium in liquid ammonia

Reviews of the reactions of the alkali metals in liquid ammonia with numerous references up to about 1937 have been given by Fernelius and Watt[1] and up to about 1950 by Watt.[2]

When oxygen is led into a liquid ammonia solution of rubidium, the peroxide, Rb_2O_2, and the superoxide or 'dioxide', RbO_2, referred to in the early literature as the tetroxide, Rb_2O_4, are formed at about –60°C.[1]

On treating a liquid ammonia solution of rubidium with ozone a gelatinous white mass of rubidium hydroxide is first formed; the blue colour of the metal solution disappears and the white precipitate redissolves to form a deep orange liquid and a second precipitate, which is similar in behaviour to the compound formed when solid potassium hydroxide is treated with ozone. The compound is considered to be an ozonide but is too unstable to isolate and study. Apparently 2/3 to 3/4 of an atom of oxygen is present per molecule of rubidium hydroxide and the formula is probably $RbOH.O$ or $(RbOH)_2O_2$.[3,4]

Finely divided rubidium, prepared by the evaporation of a solution of sublimed rubidium in dry liquid ammonia, behaves as a catalyst of weak activity in the hydrogenation of acetylene.[5]

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The monosulphide of rubidium, Rb_2S, has been prepared by the direct union of the elements in liquid ammonia.[6,7]

The rubidium polysulphide represented by the formula Rb_2S_{10}, prepared in situ in liquid ammonia in the presence of the iodide of the metal, has been potentiometrically titrated with a standard solution of rubidium in liquid ammonia at −38°C. Points of inflection on the e.m.f./composition curve indicate the formation of Rb_2S_4 and Rb_2S_2. It is impracticable to continue the titration to the monosulphide stage because the dense yellow crystals of the disulphide are almost insoluble in the solvent and react very slowly. The time taken for 1 ml. portions of the solutions to react is of the order of several hours.[8]

Féher and Naused[9] have prepared the crystalline polysulphides, Rb_2S_2, Rb_2S_3, and Rb_2S_5, by the reaction of sulphur and rubidium in liquid ammonia, and have isolated them for determination of their physical properties. The tetra- and hexa-sulphides have not been obtained in this way.

Rubidium selenide, Rb_2Se, and telluride, Rb_2Te, have been prepared from their elements in liquid ammonia.[6,7]

The relative catalytic activities of samples of nickel produced by reduction of nickel bromide, $NiBr_2$, in liquid ammonia by the action of the several alkali metals have been investigated by Watt and Mayfield.[10] The rate of solution of rubidium in liquid ammonia and the rate of reduction of nickel bromide are too rapid for accurate observation, but both rates are greater with rubidium than with lithium, sodium or potassium but not so great as with caesium. The catalytic activity of the nickel produced per unit area is practically constant for all the alkali metals.

Rubidium reacts with carbon monoxide in liquid ammonia at −60°C. to give a white precipitate of the carbonyl, RbCO.[11]

Lead reacts with rubidium in liquid ammonia solution to give an amethyst solution.[12]

A monoalkali acetylide is formed, $RbHC_2$, when acetylene is passed into a liquid ammonia solution of rubidium at −40° to −60°C. Some acetylene is reduced to ethylene.[1]

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Reactions of rubidium with organic compounds

General accounts of the reactions of the alkali metals with organic compounds have been given by Wooster,[1] Coates[2] Sidgwick[3] and Gilman.[4]

Rubidium reacts with diethyl zinc to form ethyl rubidium which has been isolated in the form, $RbEt,ZnEt_2$, m.p. 70°–75°C.[5]

Benzene or toluene reacts with rubidium in a vacuum, even at ordinary tem-

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peratures, with blackening of the metal surface; at higher temperatures, above the m.p. of the metal, a black slimy mass is formed without evolution of gas. By analogy with the reaction of caesium and benzene, the black compound is described as rubidium phenyl.[6] On treatment with water diphenyl and not benzene is formed and Grosse[5] states that the compound with caesium cannot possibly be caesium phenyl; de Postis[7] has since shown in fact that caesium reacts with benzene to give $C_6H_6Cs_6$ and with toluene to give C_6H_5-CH_2Cs.

According to Bridgman[8] a chemical reaction occurs when rubidium and petroleum ether are subjected to high pressures.

A precipitate of rubidium phenyl is obtained when rubidium in benzene is stirred with di-*n*-butyl mercury. On treatment with hydrogen, rubidium hydride and benzene are formed: $RbPh + H_2 \rightarrow RbH + C_6H_6$. The rate of reduction at room temperature and at a pressure slightly above atmospheric is shown in Table III.

TABLE III.- REDUCTION RATES OF ALKALI-METAL PHENYLS WITH HYDROGEN IN BENZENE

Compound	Average time hrs. for 90% Reduction
NaPh	1·9
KPh	0·54
RbPh	0·42
CsPh	0·2

The order of reactivity of the alkali metal phenyls is CsPh > RbPh > KPh > NaPh. Apparently this is one of the very few non-catalysed reactions of molecular hydrogen occurring at room temperature.[9]

1:1-Diphenylethylene on treatment with rubidium dimerizes and adds on rubidium.[10] The metal does not however add to tetraphenylethylene, probably owing to steric factors associated with the relatively large atomic volume of the metal compared with that of sodium. With sodium–rubidium alloy probably the sodium derivative is first formed but the final product is the rubidium compound: $Ph_2CRbCRbPh_2$.[10]

Phenylacetylene reacts with the alkali metals to form compounds of the type $PhC\vdots CM$. When 0·02 moles of the hydrocarbon in 25 ml. of ether is added to 0·01 g.-atom of the metal, the time required for reaction is 12 hr. for rubidium, 25 hr. for caesium and 40 hr. for potassium. The rubidium compound is tan coloured.

The time required for the reaction of the alkali metal phenylacetylides with benzonitrile in ether is shown in Table IV and the magnesium bromide compound is also included:

TABLE IV.- RATE OF REACTION OF METAL PHENYLACETYLIDES WITH BENZONITRILE

Compound	Time (hr.)
$PhC\vdots CMgBr$	87, 85
$PhC\vdots CLi$	57, 63
$PhC\vdots CNa$	6·5, 7·0
$PhC\vdots CK$	4·3, 4·5, 5·3, 5·1
$PhC\vdots CRb$	4·8, 4·9
$PhC\vdots CCs$	3·8, 3·9

The heavier is the alkali metal the more reactive it appears to be. There is no apparent reaction with ether during the time required for the addition of benzonitrile.[10]

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Alkali metal organic compounds of the type RM give very good yields of the corresponding acid when carbonated in boiling ether and treated subsequently with a mineral acid.[10]

Rubidium amalgam reacts with triphenylmethyl chloride in ether solution to give first the free radical, Ph_3C, which then adds to one atom of rubidium, Ph_3CRb. The deep blood-red solution and the solid powdery product resemble those of the sodium and potassium products. Air and moisture immediately decolorise the compound but if dried in the absence of these the product will redissolve in ether. In dilute solutions (1 g. of rubidium in 350–450 ml. of ether) the addition of triphenylmethyl chloride gives the dark red colour of the rubidium compound, but on shaking the colour is destroyed and does not reappear. The isolated rubidium compound, Ph_3CRb, probably contains some free radical because on treatment with water, in addition to triphenylmethane, Ph_3CH, another substance, m.p. 180–186°C. sparingly soluble in benzene, probably a peroxide, is obtained.[5]

The alkali metal compounds of benzophenone react with *n*-butyl chloride at relative rates which show the order of activity to be: $Cs > Rb > K$.[10]

A grey coating forms on the surface of rubidium when placed in a mixture of paraffin oil and carbon tetrachloride.[6]

Rubidium in small amounts or its sulphate or nitrate behaves as a catalyst in the oxidation of natural gas by liquid-phase contact with 80–98% sulphuric acid or fuming acid at 240–320°C. to produce methyl alcohol, formaldehyde and acetaldehyde. The catalysts are dispersed in the acid, the metal dissolving, probably as its sulphate.[11]

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RUBIDIUM ALLOYS

The behaviour of rubidium with lithium, sodium and potassium has already been described under the heading of 'Alloys' with the appropriate alkali metal.

The system rubidium–caesium has been studied by several workers. Goria[1] by means of thermal analysis, found a eutectic at –39°C. with approximately 13% of rubidium, but no evidence of any compound, not even unstable ones, nor of any solid solutions.

According to Böhm and Klemm[2] the rubidium–caesium system forms a mixed crystal containing 31 at.-% of rubidium: thermal analyses and *X*-ray examinations were used in this investigation and lattice constants were measured at –70°C. Complete miscibility is found in the solid and molten state.

Rinck[3] has prepared composition–conductivity diagrams for the rubidium–caesium system, all of the experimental work being carried out in an evacuated system. The composition-conductivity curves obtained from data at 0°C. and −39°C. are both continuous with a minimum point at the composition RbCs. The two elements form an uninterrupted series of solid solutions, the minimum melting point, 9°C., corresponding with the composition RbCs. These results differ entirely from Goria's which were obtained by working in an atmosphere of an inert gas and not in an evacuated system. Rinck considers that the system studied by Goria was in fact Cs–Rb–O–OH and not Rb–Cs.

Hara[4] has determined the freezing points of a number of completely isomorphous bimetallic systems, including the rubidium-caesium system, and plotted freezing point-composition curves. The composition of the system at the minimum f.p. is represented by the formula RbCs.

Geguzin and Pines[5] have prepared calculated and experimental equilibrium diagrams for a number of binary systems including rubidium-caesium. Equations involving the melting point of each of the two metals, the heats of mixing in the liquid and solid solutions and the concentrations of the liquid and solid solution have been used to predict the shapes of the liquidus and solidus curves of a number of diagrams. The temperature of the point of equal concentration has been calculated from the equation:

$$Tm = T_A - (T_B - T_A)\frac{x^2}{1-2x}$$

where Tm is the temperature of melting required, T_A, T_B the melting points of the two pure components and x the experimental value for the concentration at Tm. The following values are given: T_A(caesium), 299°K.; T_B (rubidium), 312°K.; x, 0·42; Tm (calculated) 284·7°K.; Tm (experimental) 278°K.

Henry and Raynor[6] have applied the general metallurgical implications with respect to the cohesion of alloys[7] to the particular case of the alkali metals and give calculations which show that solid solution formation is restricted in all the possible alkali metal systems except rubidium-potassium, rubidium-caesium and potassium-caesium for which extensive solid solutions exist. Further extension of the theory to include the liquid state enables the relative magnitudes of the liquidus depressions to be accounted for in the system rubidium-caesium.

The existence of intermetallic compounds in the vapour state has been shown by spectra of the alkali metals and of their alloys with each other.[8,9] Rubidium and caesium combine with each other in the vapour state; the observed bands lie near the principal series lines of the constituent atoms.

The rubidium-gold system has been investigated by Ehrhorn *et al.*[10] Finely divided gold and purified rubidium are heated at 200°–220°C. for 12–18 hr. to cause a reaction to occur in an atmosphere of argon at 720 mm. By heating in vacuo at 150° to 200°C. for 5 hr. or more a black mixed phase is produced; this is decomposed by heating at 250° to 300°C. for 10 to 20 hr. The preparation is complete when no more rubidium distils off. The residue is pure dark green and contains only 17–19% of rubidium. Larger crystals have a light green lustre and are brittle. The X-ray diagram is quite different from that of either constituent. The compound $RbAu_2$ is not as stable in air as is the potassium compound but it can be readily handled.

The space occupied by the alkali metals in the above alloys is much less than that occupied by the pure metals; this is considered to be due to compression.[11]

In the rubidium-cadmium system, the intermediate phase poorest in rubidium is the crystalline cubic compound, $RbCd_{13}$, having the lattice side a = 13·88 A. There are 112 atoms in the unit cell. This composition has been confirmed by *X*-ray, density and analytical data, which do not agree with the formulae, $RbCd_{11}$ or $RbCd_{12}$, given in the literature. The alkali metal is surrounded by 24 equally distant cadmium atoms. Powder diagram data are given by the authors.[12]

The complete phase diagram for the rubidium-mercury system has been constructed on the basis of thermal analysis by Biltz, Weibke and Eggers.[13] Eight compounds are shown: Hg_9Rb, ·4·52% Rb, m.p. 67°C.; Hg_6Rb, 6·63% Rb, m.p. 132°C.; Hg_9Rb_2, 8·45% Rb, m.p. 162°C.; $Hg_{18}Rb_5$, 10·58% Rb; Hg_7Rb_2, 10·85% Rb; Hg_2Rb, 17·56% Rb, m.p. 256°C. decomp.; Hg_4Rb_3, 24·21% Rb, m.p. 170°C.; Hg_8Rb_7, 27·15% Rb, m.p. 157°C. See Fig. 1.[14]

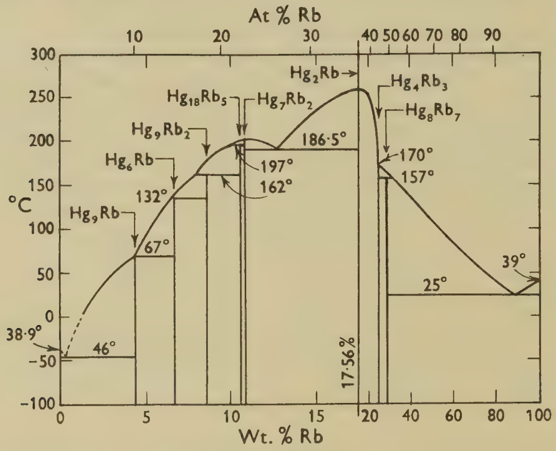

FIG. 1.- THE SYSTEM Hg-Rb

The light alkali metals do not form compounds as rich in mercury as the heavy alkali metals. Also comparable compounds of mercury with the alkali metals have lower melting points with increasing atomic number of the alkali metal.

Grube[15] has discussed the various methods used for the detection of intermetallic compounds in alloy systems and describes the rubidium-mercury system. *X*-Ray investigations, thermal expansion determinations, measurement of electrical resistance and of magnetic properties give useful information for detecting compound formation. Many graphs and diagrams are given by the author.

A short account of the theory of the molecular constitution of amalgams is given by Schulze[16] with many tables and diagrams giving published data up to 1925 on the electrical conductivity of amalgams and the effects of composition and temperature. Typical values for electrical conductivity are given in Table V.

TABLE V.- ELECTRICAL CONDUCTIVITY OF RUBIDIUM AMALGAM

At.-% Rb	Wt.-% Rb	Specific Conductivity at 18°C.	Relative Conductivity				
			0°	20°	40°	60°	80°
0·000	0·000	$1·0462\times10^4$	1·000	1·000	1·000	1·000	1·000
0·092	0·039	$1·0400\times10^4$	-	0·9941	0·9948	0·9941	0·9937
0·175	0·074	$1·0332\times10^4$	0·9856	0·9879	0·9888	0·9884	0·9874
0·459	0·196	$1·0162\times10^4$	0·9714	0·9713	0·9707	0·9697	0·9683

The partial molal free energy of rubidium in the compound $RbHg_{12}$ has been measured by the e.m.f. of a galvanic cell, the electrodes of which consist of the electropositive metal and the liquid amalgam saturated with the mercuride. A value of −24·8 kg.-cal. has been obtained by Gerke[17] for rubidium.

The data in Table VI are given by Semenchenko *et al.*[18,19] for the surface tension of rubidium–mercury alloys.

TABLE VI.- SURFACE TENSION OF RUBIDIUM–MERCURY ALLOYS

Concentration g.-atom Rb/l.	Surface Tension dyne/cm.
0·000756	405
0·00128	401
0·00148	386
0·00189	324
0·00398	322
0·00715	280
0·01181	292
0·0198	255
0·0267	258
0·0864	237

The solid-solubility effect of metallic surface friction has been used by Umeda and Nakano[20] to assist in the construction of some phase diagrams. The surface coefficient of friction, μ, is determined as a function of temperature noting the temperature when μ becomes zero, *i.e.* at the eutectic point of the binary system. The binary mixtures which show this effect, including rubidium–mercury, are given.

The rates of reaction between alkali metal amalgams, (rubidium amalgam included) and acid solutions are shown to be dependent on the hydrogen ion concentrations, on the rate of stirring, and on the volume and surface area of the amalgams. Good duplication of results is obtained if platinised platinum is used as the other electrode but smooth platinum gives varying results.[21]

Hohmann[22] has investigated the action of the alkali metals on silicon and germanium. The latter are heated at 600° to 700°C. in an inert atmosphere with an excess of the alkali metal. When the reaction is complete excess metal is distilled off in vacuo leaving behind crystalline compounds with one atom of the alkali metal combined with one atom of silicon or germanium. The compounds are decomposed by acids, alkalis and water. Whereas the sodium compound NaSi decomposes on further heating in a vacuum, the heavier alkali metal compounds form KSi_8, $RbSi_8$, $CsSi_8$ and KGe_4, $RbGe_4$, and $CsGe_4$. It has been shown more recently by *X*-ray methods that the compounds obtained by thermal decomposition of potassium, rubidium and caesium silicides at 10^{-3} mm. Hg at about 400°C. are KSi_6, $RbSi_6$ but $CsSi_8$.[23]

Experimental difficulties arise in the preparation of phosphorus and arsenic compounds of rubidium; not only are the substances sensitive to air and moisture, they also attack the container materials and have high dissociation pressures. With phosphorus in particular, the preparation of homogeneous substances is very difficult. The compound, Rb_3P, has not yet been prepared; Rb_2P_5 is described as a polyanionic substance. The arsenic compound, Rb_3As, is said to have a salt-like structure.[23]

Just as with potassium vapour and red phosphorus under certain conditions small black needles of approximate composition KP_{10} are obtained, so also is a similar compound obtained with rubidium.[23]

A number of phases are shown to exist in the rubidium–antimony system; antimony-rich structures appear with the composition, Rb_3Sb_7 or Rb_2Sb_5; Rb_3Sb has the crystal lattice of a salt-type structure; the sum of the atomic volumes

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of the two components is 177, the calculated value for the ions (*i.e.* salt-type) being 106 and for the intermetallic compound 101; the experimental value is 114. It cannot be deduced from the molar volume whether the compound is salt-like or intermetallic.[23]

The rubidium–bismuth system contains a number of phases.[23] The crystal lattices of the Rb_3Bi and $RbBi_2$ compounds show an intermetallic phase structure *i.e.* a cubic structure; the molar volume of the Rb_3Bi compound being much less than the sum of the atomic volumes of rubidium and bismuth. The sum of the atomic volumes is 180, the calculated value for the ions (*i.e.* assuming a salt-like structure) is 120 and that for an intermetallic compound 105. The experimental value is 109. For the compound $RbBi_2$ the sum of the atomic volumes is 95, the calculated value for the ions (*i.e.* a salt-like structure) being 74 and for an intermetallic compound 67; the experimental value is 66·6, intermediate between the two. The greater the difference in the electronegativity of the two components in a binary system the greater is the contraction of the volumes of the free ions. The electronegativity differences plotted against % contraction of the free atoms are greater for the cubic structures than for the hexagonal structures.

Klemm[23] has recently described the properties of the metalloids and their compounds with the alkali metals. Base metals such as the alkali or alkaline earth metals form salt-like compounds with the typical non-metals, chlorides, oxides, etc. Metals form intermetallic compounds with each other. The purpose of Klemm's research was to study the effect of adding to a base metal another element which is varied gradually from a typical non-metal through a metalloid to a metal. It appears to be unimportant for the properties of these compounds whether they appear in a more salt-like or a more alloy-like structure. The crystallographic structure is primarily determined by the proportions of the compounds, their size and polarisability. The absolute values of the electronegativity and electronegativity differences are apparently more important in deciding the properties of the compound. The elements used with lithium, sodium, potassium, rubidium, and caesium to illustrate his points are silicon, germanium, carbon, tin, lead, phosphorus, arsenic, antimony and bismuth.

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SECTION LXVI

RUBIDIUM HYDRIDE

By N.M. HOPKIN

Rubidium hydride is prepared[1] by heating rubidium carbonate with magnesium in the presence of hydrogen. The reaction with magnesium takes place at 260°C. and the rubidium vapour combines with the hydrogen at 620–680°C.; after 49hr. nearly 90% of the rubidium is converted into the hydride. Rubidium deuteride[2,3] can be prepared by reducing deuterium oxide with iron and causing the deuterium to react with freshly distilled rubidium. The reaction with deuterium can take place at 360°C., but it is slower than that with hydrogen. The dissociation pressures can be calculated from the equation:-

$$\log p = (a/T) + b,$$

where a and b are $-4533{\cdot}5$ and $9{\cdot}20$ for the hydride, and $-2664{\cdot}0$ and $6{\cdot}07$ for the deuteride, respectively. These differences suggest a method for separating the two isotopes. Rubidium hydride can also be prepared[4] by mixing the molten metal with finely divided sodium hydride and 0·1 to 1·0wt.-% of a fatty acid containing more than 8 carbon atoms, e.g. stearic, oleic, or palmitic acid etc. or one of the metal salts. Hydrogen is introduced and the reaction maintained at 200–450°C. A hydrocarbon with more than 8 carbon atoms, e.g., *iso*propylbenzene, which forms a hydrocarbide with the alkali metal, may be used instead of the fatty acid. In this case the vapours of the hydrocarbon are introduced into the stream of hydrogen entering the reactor. Rubidium hydride has also been prepared[5] by distilling finely divided pure rubidium into the reaction vessel and allowing it to react with pure hydrogen generated *in situ* by the decomposition of potassium hydride. The rubidium reacted below its m.p. at the rate of 0·062 c.c. of combined hydrogen per sq. cm. of surface area per hr. at 100°C. The hydride does not dissolve in metallic rubidium up to 150°C. Pure hydrides free from metal can be prepared at 3 atm. and 50°C.

The density[6] of rubidium hydride has been determined pycnometrically and found to be 2·60 ± 0·07. The previous values given by Moissan are too low. When hydrogen is taken up by rubidium considerable contraction, 40·7%, of the lattice takes place; it is greater in the case of the alkali metals than it is with the alkaline earth hydrides. The radius of the H ion is 1·45 A.

The latent heat[7] of sublimation has been calculated for rubidium hydride from spectroscopic and thermochemical data; the following figures are given:- the heat of formation of rubidium hydride is 12·0, the latent heat of sublimation 40·4 and the heat of dissociation 43·8kg.-cal./mole. The figures for cæsium hydride are similar, but the latent heat of sublimation is slightly lower.

The calculated dipole moment[8] of rubidium hydride is 7·73 debyes, and the corresponding lattice energy[9] is 161kg.-cal. when Hyleeraas' value for the electron affinity for H^- of 17 ± 1kg.-cal. is used. In studying the photochemical decomposition[10] of alkali hydrides it was found that rubidium hydride showed maximal absorption at wave-lengths of 2020 and 2680 A.

The interatomic R–H distance[11] in the rubidium hydride molecule has been calculated accurately from spectroscopic data and Stevenson gives a value of 2·368 A. The dissociation pressure of rubidium deuteride[12] increases more rapidly with increasing temperature than does that of rubidium hydride. The dissociation pressure is within ±2 mm. of mercury up to 220°C., but at 320°C. it is 61·8 mm. of mercury for rubidium deuteride and only 33·8 for rubidium hydride. The experimental values for rubidium hydride over the temperature range 245·5°C.–415·5°C. fit the equation:-[13]

$$\log p = -\frac{5680}{T} + 11{\cdot}80$$

The heat of formation for rubidium hydride was calculated to be 13,480 g.-cal. with an error of less than ±1·5%.

Application

If rubidium is heated with a metal halide above the m.p. of the halide in the presence of hydrogen, but below the dissociation temperature of rubidium hydride, a stable solid solution[14] of the hydride is formed in the halide. This is less hazardous to handle than the free hydride and can be used as a drying or a reducing agent.

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SECTION LXVII

RUBIDIUM OXIDES AND HYDROXIDE

By L. F. WILSON

RUBIDIUM OXIDES

The following oxides of rubidium are known:

Rb_2O – rubidium monoxide.
Rb_2O_2 – rubidium dioxide or peroxide.
Rb_2O_3 – rubidium sesquioxide or peroxide–superoxide.
RbO_2 – rubidium superoxide or tetroxide.

Rubidium monoxide is prepared by controlled oxidation of the metal in air or oxygen. The oxidation must be prevented from proceeding past the monoxide to the higher oxides;[1] an excess of rubidium is used and the excess metal is distilled off in vacuo. The reaction of rubidium metal with mercuric oxide also produces rubidium monoxide.

The compound is colourless, or very pale yellow, in the cold but becomes deep-yellow when hot. The crystal system is cubic, $a = 6{\cdot}742$ A., and the structure is of the antifluorite type with the rubidium ions occupying the positions of the fluorine ions, and the oxygen ions the calcium positions, in the fluorite lattice.[1]

Rubidium dioxide is more correctly named rubidium peroxide since it reacts with water to yield hydrogen peroxide. The compound is made by controlled oxidation of rubidium metal or the monoxide, either in air or in liquid ammonia solution. Rubidium peroxide oxidises readily in air to give the superoxide. The reaction $Rb_2O_2 + \frac{1}{2}O_2 \rightleftharpoons Rb_2O_3$ is reversible only within certain temperature limits above which association does not take place.[2] The melting point is 570°C., the dissociation temperature at atmospheric pressure is 1011°C. and the heat of formation is 118·1 kg.-cal./mole.[3]

Rubidium sesquioxide is prepared as a black solid by controlled oxidation of rubidium metal in liquid ammonia solution or by oxidation of the peroxide at 200°C. and low partial pressures of oxygen.[4] It is also formed by thermal decomposition of the superoxide at high temperature.

Rubidium sesquioxide melts at 489°C.; the dissociation temperature is 838°C., and the heat of formation is 126·0 kg.-cal./mole.[3] The density is 3·53 and the compound crystallises in the cubic system, $a = 9{\cdot}30$ A.[4] The structure is of the anti-thorium phosphide, Th_3P_4, type and the space group is T_d^6. Twelve oxygen groups are in the 12*a* positions and the rubidium ions occupy the 16*c* positions. Magnetic susceptibility measurements suggest that the true formula is Rb_4O_6 or $Rb_4(O_2)_3$. One oxygen group carries a double negative charge and the other two carry single negative charges, the rubidium–oxygen distances being 3·54 and 2·95 A.

Rubidium sesquioxide and cæsium sesquioxide are characterised by being very dark in colour whereas sodium and potassium sesquioxides are colourless. The colour of these compounds probably depends on the crystal structure. The electronic distribution in the crystal lattice has been described in terms of semi-localised orbitals and an explanation of the dark colour has been suggested.[5,6]

Rubidium superoxide. Superoxide formation occurs most readily with the largest and most electropositive metals and rubidium and caesium superoxides are obtained as the final oxidation products of the metals in air. Rubidium superoxide is also prepared by oxidation of the lower oxides in air, or by prolonged oxidation of the metal in liquid ammonia solution.[7]

Rubidium superoxide reacts with water to form hydrogen peroxide and oxygen. The melting point is 412°C., the dissociation temperature is 1157°C., and the heat of formation is 137·6 kg.-cal./mole.[3] Thermal decomposition to rubidium sesquioxide and oxygen occurs at high temperature.[2] Rubidium superoxide is paramagnetic, the magnetic susceptibility being $42{\cdot}2 \times 10^{-6}$ and $13{\cdot}0 \times 10^{-6}$ at −183°C. and 25°C. respectively.[7] The compound crystallises in the tetragonal system, $a = 6{\cdot}00$, $c = 7{\cdot}03$ A., and the density is 3·06. The structure is comparable to that of calcium carbide and demonstrates clearly the presence of O_2^- ions. In the structure a face-centred, tetragonal lattice of rubidium ions is interpenetrated by a similar face-centred lattice of O_2^- ions to form a distorted sodium chloride type lattice.

Other rubidium oxides. Alkali metal oxides are also formed by the spontaneous oxidation of amalgams.[8] Rubidium amalgam reacts completely with oxygen at room temperature in four to seven days to give oxides with the composition $Rb_2O_{2\cdot9}$–$Rb_2O_{3\cdot5}$. The rubidium oxides thus formed oxidise some of the mercury of the amalgam to mercuric oxide.

The reaction at −30°C. between finely-ground rubidium hydroxide and oxygen containing 8–9% of ozone yields a yellow coloured product which decomposes in water with evolution of oxygen and also liberates iodine from an acidified potassium iodide solution.[9] The coloured product can be extracted with liquid ammonia and evaporation of the solution to dryness gives a reddish-brown solid containing 40–67% of rubidium ozonide, RbO_3, mixed with rubidium hydroxide. The presence of the hydroxide is due to its appreciable solubility in liquid ammonia. The ozonide reacts with water to give rubidium hydroxide and oxygen, probably according to the equations:

$$RbO_3 + H_2O \rightarrow Rb^+ + OH^- + OH + O_2;$$
$$2OH \rightarrow H_2O + \tfrac{1}{2}O_2.$$

At room temperature the ozonide decomposes slowly to rubidium superoxide and oxygen. *X*-Ray diffraction studies show that the crystal structure is similar to that of sodium azide, NaN_3.

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RUBIDIUM HYDROXIDE

Rubidium hydroxide is commonly prepared by electrolysis of an aqueous

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solution of rubidium chloride. Two types of cell have been used: those in which the anode and cathode are in separate compartments, and those similar to the Castner–Kellner design. In the latter the cathode is mercury and a rubidium amalgam is formed which is in turn decomposed by water to give rubidium hydroxide.[1,2] Two electrolyses are necessary to produce a hydroxide free from chloride, and efficiencies up to 98% conversion of chloride to hydroxide have been reported.[2] If a glass cell is used the hydroxide produced contains appreciable amounts of sodium silicate arising from the attack on the cell by the alkali. The electrolysis of rubidium chloride in a cell consisting of two U-tubes connected in series is claimed to produce rubidium hydroxide of high purity.[3]

The melting point of rubidium hydroxide is 383°C. and the density of the molten hydroxide between 690°C. and 920°C. is represented by the equation $\rho = 3{\cdot}11-0{\cdot}00078T$.[4] The limiting conductivity of rubidium hydroxide solution is 270·4.[5] The density, equivalent conductance and viscosity, relative to water, of aqueous rubidium hydroxide solutions at 25°C. are given in Table I.[5,6]

TABLE I.- DENSITY, EQUIVALENT CONDUCTANCE AND VISCOSITY OF AQUEOUS SOLUTIONS OF RUBIDIUM HYDROXIDE

Concentration of RbOH (moles/litre)	Density ρ	Equivalent conductance Λ	Viscosity, centipoises
0·002118	0·9973	267·3	
0·002482	0·9973	266·3	
0·003124	0·9974	266·0	
0·004206	0·9975	265·0	
0·007394	0·9978	262·4	
0·009287	0·9980	261·2	
0·011594	0·9982	260·7	
0·0918	1·0058		1·0087
0·1746	1·0133		1·0163
0·480	1·0415		1·0461
0·683	1·0593		1·0678

The viscosity of rubidium hydroxide solutions is less than that of corresponding potassium hydroxide solutions; this accords with the lower hydration of the rubidium ion relative to the potassium ion.[6] The neutralisation of acids by alkalis in aqueous solution can be followed by viscosity measurements; with rubidium hydroxide and sulphuric acid a minimum in the viscosity occurs at the neutral point.[7]

Measurements of the intensity of resonance radiation emitted by hydrogen–air flames contaminated with small quantities of the alkali metal hydroxides indicate that the relative stability of the hydroxides decreases in the order LiOH, CsOH, RbOH, KOH and NaOH.[8]

The lattice energy of rubidium hydroxide is 147 kg.-cal./mole.[9] The compound crystallises in the orthorhombic system with unit cell dimensions $a = 4{\cdot}15$A., $b = 4{\cdot}30$A. and $c = 12{\cdot}2$A.[10] and has the same structure as sodium hydroxide.

The countercurrent electrophoresis of rubidium hydroxide solution has been used for the partial separation of ^{85}Rb and ^{87}Rb.[11] The ratio of the mobilities of the two ions is 1·0056. At a potential of 2300 V., and 80°C., the ^{85}Rb concentration in the cathode compartment increases from 72·2 to 73·8% in two hundred hours.

The use of rubidium and caesium hydroxides in alkaline storage batteries has been proposed.[12] The hydroxides are substituted, partially or completely, for sodium and potassium hydroxides and more efficient operation at low temperatures is claimed.

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SECTION LXVIII

RUBIDIUM FLUORIDES

By L. F. WILSON

Rubidium fluoride, RbF, has a melting point of 775°C. and a boiling point of 1410°C.[1] The vapour pressure of the salt between 1163°C. and the boiling point is given by the expression

$$\log p_{(\text{atm.})} = \frac{-40{,}000}{4{\cdot}57T + 5{\cdot}243}.$$

Observed values of the vapour pressure in this temperature range are given below.

T(°C.)	p(mm.)
1163	96·9
1166	98·9
1197	124·0
1251	233·6
1256	233·6
1345	499·0
1351	502·9
1356	522·3
1402	729·4
1404	729·4
1410	754·6

Vapour density measurements for rubidium fluoride indicate that the salt exists as individual molecules in the vapour state.[2]

The heat of formation of rubidium fluoride is 132·8 kg.-cal./mole.[3] The standard free energy of hydration is 174 kg.-cal./mole,[4] and the heat of solvation 186 kg.-cal./mole.[5] From the ultra-violet absorption spectrum of rubidium fluoride the dissociation energy is calculated as 125 kg.-cal./mole.[6]

The solubility of rubidium fluoride, and of rubidium hydrogen fluoride, in acetone is negligible.[7] The salt dissolves to some extent in bromine trifluoride with the formation of $RbBrF_4$.[8]

Rubidium fluoride, like the fluorides of cæsium and potassium, forms complex fluorides with many other metal fluorides. The results of thermal analysis and *X*-ray diffraction studies in systems involving rubidium fluoride are given below.

RbF–KF.	Potassium fluoride, m.p. 856°C., and rubidium fluoride, m.p. 780°C., form a continuous series of solid solutions. No compounds are formed in the system.[9]
$RbF–MgF_2$.	The compounds RbF,MgF_2 and $2RbF,MgF_2$, m.p. 912°C. and 792°C. respectively, are formed, and eutectics are shown at 37·5 mol.% RbF, m.p. 883°C., and 81 mol.% RbF, m.p. 686°C.[9] (Mixtures containing

	50–75% of RbF are greenish in colour.[10] In the ternary system $KF–MgF_2–RbF$, solid solutions are formed between any proportions of KF,MgF_2 with RbF,MgF_2 and of $2KF,MgF_2$ with $2RbF,MgF_2$.[9]
$RbF–BaF_2$.	No compounds are formed; the system shows a eutectic at 35 mol.% RbF, m.p. 660°C.[11]
$RbF–BeF_2$.	The compound RbF,BeF_2, m.p. 520°C. is formed and the system shows a eutectic at 28 mol.% RbF, m.p. 445°C.
$RbF–YF_3$.	The compound $3RbF,YF_3$, m.p. 1064°C., is formed and a eutectic occurs at 91 mol.% RbF, m.p. 752°C.[13]
$RbF–LaF_3$.	The incongruently melting compound RbF,LaF_3 m.p. 684°C., is formed, and a eutectic occurs at 79·5 mol.% RbF, m.p. 582°C.
$RbF–ErF_3$.	The compound $3RbF,ErF_3$, m.p. 1034°C., is formed and there is a eutectic at 732°C.[14]
$RbF–PrF_3$.	The compound $3RbF,PrF_3$, m.p. 797°C., is formed.[14]
$RbF–SmF_3$.	The compound $3RbF,SmF_3$, m.p. 916°C. is formed and a eutectic is shown at 700°C.[14]
$RbF–ThF_4$.	The compounds $3RbF,ThF_4$, RbF,ThF_4 and $RbF,3ThF_4$ m.p. 974°C., 852°C. and 1004°C. respectively, are formed. Eutectics occur at 85, 63, 56 and 20 mol.% of RbF, m.p. 664°C., 762°C., 848°C. and 1000°C. respectively.[15] The ternary system $KF–ThF_4–RbF$ shows an uninterrupted series of solid solutions between the potassium complex fluorides and the corresponding rubidium compounds.

Dergunov[13,14] has noted that the tendency to form complex fluorides of the type $3M'F,M'''F_3$ where M' is an alkali metal and M''' a trivalent metal, falls with increasing radius of the trivalent metal ion and the thermal stability increases with increasing radius of the alkali metal ion.

Complex fluorides of the type $RbM''F_3$, where M'' represents calcium, magnesium or zinc, are formed by the reaction of rubidium fluoride with the oxides of the divalent metals at temperatures between 500°C. and 800°C.[16] The reaction between rubidium fluoride and strontium oxide yields a mixture of rubidium oxide and strontium fluoride. The double fluorides may also be synthesised from the component fluorides. *X*-Ray powder diffraction studies show that their structures are all modifications of the perovskite structure. $RbCaF_3$ crystallises in the cubic system, $a = 8{\cdot}69$ A.; $RbZnF_3$ is tetragonal, $a = 8{\cdot}69$, $c = 7{\cdot}30$ A.; and $RbMgF_3$ is monoclinic, $a = b = c = 8{\cdot}17$ A. and $\beta = 98°30'$.

Rubidium fluoride also forms complex compounds with other rubidium salts. The compounds that have been characterised are:

RbF,Rb_2CO_3.[17]
RbF,Rb_2SO_4.[17]
RbF,Rb_2CrO_4.[18]
RbF,Rb_2MoO_4.[18]
RbF,Rb_2WO_4.[18]
$RbF,Rb_2Ti_2O_5$.[19]

A study of the system $RbF–MoO_3$ shows that the congruently melting compound $Rb_3MoO_4F_3$ is formed.[18] The compound crystallises in the cubic system and hydrolyses rapidly to form Rb_3MoO_4F.

Rubidium fluoride forms a well-defined double compound with osmium tetroxide, $OsO_4,2RbF$.[20] The compound is unstable and rapidly dissociates into rubidium fluoride and osmium tetroxide.

Reaction of fluorine gas with rubidium chloride, as with potassium and caesium chlorides, produces compounds that contain active fluorine. These compounds have been called '*perfluorides*', and for rubidium and caesium a limiting formula of MF_3 is reached.[21,22] Passage of fluorine gas, free from hydrogen fluoride, over rubidium chloride at 140°–220°C. gives a perfluoride with a composition approaching RbF_3. During the reaction the weight of the rubidium chloride first decreases to a minimum and then increases. If the product is allowed to cool at the minimum weight no further addition of fluorine occurs on heating. The primary reaction is probably the formation of rubidium fluoride, in an unstable form, which can either transform to the stable fluoride or combine with more fluorine to give the perfluoride. The reaction of fluorine with mixtures of alkali halides gives rise to compounds such as KF_3,RbF_3.

The perfluorides are white, anhydrous powders. They liberate fluorine with moist air or acids. Reaction with water gives oxygen and with ammonia gives nitrogen. Iodine is liberated from potassium iodide solution. Anhydrous nickel chloride reacts with rubidium perfluoride to give the compound Ni_3RbF_6. A perfluoride with the composition RbF_2 is optically isotropic. The same compound has a magnetic susceptibility of -14×10^{-6} and -11×10^{-6} at 20°C. and −183°C. respectively. A perfluoride of composition $RbF_{2\cdot53}$ loses fluorine when heated to 265°C.[21,22]

Acid Fluorides of Rubidium

The simple acid fluoride, rubidium hydrogen fluoride or "bifluoride", RbF,-HF, can be prepared by the action of a slight excess of aqueous hydrofluoric acid on rubidium carbonate.[23] (If glass apparatus is used a small quantity of poorly-soluble rubidium fluorosilicate, Rb_2SiF_6, is also formed.[24]) The solution is concentrated and on cooling sets to a hard white mass of rubidium hydrogen fluoride. The saturation vapour pressure of hydrogen fluoride above the salt is low, but thermal decomposition into rubidium fluoride and hydrogen fluoride takes place below red heat. The melting point is 204–5°C. and the salt is not hygroscopic.[23] The infra-red absorption and reflection spectra of potassium hydrogen fluoride and rubidium hydrogen fluoride are similar and the two compounds are isomorphous.[25]

The hyper-acid fluoride, RbF,2HF, is prepared by dissolving the simple acid fluoride in 36–40% aqueous hydrofluoric acid and evaporating the solution at room temperature in a desiccator.[23] The melting point is 51·6°C. and even in the fused state at 60°C. the rate of loss of hydrogen fluoride is slow; at 100–110°C. the loss of hydrogen fluoride is appreciable. The salt is a colourless crystalline compound, deliquescent and easily soluble in water.

The higher acid fluorides RbF,3HF and RbF,3·5HF have also been described.[26] RbF,3HF is made by dissolving the hyper-acid fluoride in anhydrous hydrogen fluoride and cooling the solution in a solid carbon dioxide–acetone cooling bath. RbF,3HF separates from hydrogen fluoride–rubidium fluoride solutions in which the hydrogen fluoride content is in the range 35–40%.

RbF,3·5HF separates from mixtures of rubidium and hydrogen fluorides containing approximately 45% of hydrogen fluoride. The salt forms hard, clear, granular crystals and the melting point is between 34°C. and 40°C. The vapour pressure of hydrogen fluoride just above the melting point is fairly low and it is possible to maintain the compound in a liquid state for some time without appreciable loss of hydrogen fluoride. Some evidence exists for the formation of a higher acid fluoride, RbF,4·5HF; however it decomposes very easily into RbF,3·5HF and hydrogen fluoride.

The acid fluorides of rubidium all dissolve readily in water to give strongly acid solutions which attack glass. They resemble the corresponding potassium salts in thermal stability and in general behaviour.

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SECTION LXIX

RUBIDIUM CHLORIDE

By L. PRATT

The small quantities of rubidium and cæsium found in carnallite can be obtained by precipitating them as the silicomolybdates. The precipitate is heated in a stream of hydrogen chloride to leave the mixed chlorides.[1,2] Rubidium chloride can also be partly concentrated from carnallite by fractional crystallization,[3] and it is extracted from plant ash[4] by precipitation as the perchlorate from a hydrochloric acid solution of the ash, the perchlorate being subsequently converted to the chloride by heating. The chloride is also produced by passing hydrogen chloride into a slurry of a solid rubidium salt in its saturated solution.[5]

Mixtures of rubidium and cæsium chlorides can be separated by fractional precipitation from ethanol solution by hydrogen chloride; the cæsium chloride remains in solution and can be precipitated as the silicomolybdate or as the double salt with antimony trichloride.[2,6] The chlorides can also be separated by sublimation, since cæsium chloride is much more volatile than rubidium chloride in a vacuum at 440°C.[7]

Since these two chlorides are more soluble in the presence of hydrochloric acid than is sodium chloride, it is possible to separate either of them from a much greater amount of sodium chloride by dissolving the mixture in strong aqueous hydrochloric acid, and saturating the solution with hydrogen chloride. This precipitates most of the sodium chloride, and the rest of it can be removed almost completely by redissolving the impure rubidium or cæsium salt in ethanolic hydrogen chloride and again saturating with hydrogen chloride.[8] The same method cannot be used to separate rubidium and potassium chlorides because these two salts form mixed crystals (see page 2202). Fujiwara[9] has discussed the theory of this type of selective crystallization.

Barrer and Sammon[19] showed that rubidium can be separated completely from sodium and potassium, as chloride, by means of silver analcite, an ion sieve reagent. The same process will separate rubidium and cæsium if methanol or ethanol is used as the solvent. Kayas[11] achieved a complete separation of these four alkali metals by selective adsorption on a column of Amberlite IR 100 cation exchange resin, the ions being eluted with hydrochloric acid. Cabell and Smales[12] obtained a more rapid separation of potassium, rubidium and cæsium as chlorides by means of a column of Zeocarb 315 cation exchange resin, one metre long. The cations were eluted with hydrochloric acid solutions of strengths 0·1 M., 0·5 M. and 1·0 M. respectively. A much better separation of alkali metal cations was found by Smit,[13] who used a very short column of ammonium phosphomolybdate. The advantage of using inorganic solids as cation exchange agents in the separation of alkali metals was emphasised by Amphlett *et al.*[14] who also found a good separation of the ions on zirconium phosphate, eluted with ammonium nitrate and nitric acid solutions. Small quantities of alkali cations can be separated by paper chromatography.[15,16]

A pure sample of rubidium chloride can be made[17] by passing chlorine into an aqueous solution of the bromide. The bromine is boiled off and the chloride crystallized out and dried for four days in a vacuum at a temperature which is slowly raised to 350°C. The salt is melted in a vacuum and cooled so as to solidify from the outside, the central core being discarded.

The amount of rubidium in the chloride can be estimated by flame photometry,[18] by arc emission spectroscopy[19] or by other spectrochemical methods.[20] Small amounts (0·01 mg. to 0·01 γ) of rubidium and cæsium in minerals can be determined by neutron activation analysis.[12,21]

Crystalline Rubidium chloride.

Single crystals can be prepared from the molten salt.[22,23] Crystals grow from aqueous solutions more quickly when small amounts of other ions are present.[24] The melting point has been given as 715°C.,[25] 722°C.[25] and 726°C.,[27] but the latest value, 722 ± 2°C.,[17] is probably to be preferred. The heat of fusion is 4·8 kg.-cal./mole[28] and values of the free energy of formation over the range 25–100°C. have been given.[29] The heat of formation of the lattice was calculated to be 162·0 kg.-cal./mole by Huggins,[30] a value equal to that calculated by using the Born cycle.[31]

The density at 25°C. is 2·803 g./c.c.[32] The coefficient of compressibility $6{\cdot}52 \times 10^{-6}$ cm.^{2}/kg. compares with a calculated value of $5{\cdot}82 \times 10^{-6}$.[33] Bridgman[34] found that the decrease in volume under a pressure of 50,000 kg./cm.^{2} was 0·2768 at room temperature (~ 25°C.) and 0·2714 at −78°C. This decrease is not entirely due to compression of the lattice, since a transition occurs between 4000 and 5000 kg./cm.^{2}. *X*-Ray diffraction studies of rubidium chloride under pressure[35,36] show that at 7500 kg./cm.^{2} the crystal structure is of the cæsium chloride type, which for large cations is denser than the sodium chloride type shown by rubidium chloride under normal pressures.

The length *a* of the side of the unit cell cube in the normal structure has been given as 6·571 A.[37] and also as 6·591 A.,[38] the latter being extrapolated from values of the dimension of the unit cell in mixtures of rubidium chloride and bromide. The most reliable value is probably that given by Wyckoff,[39] $a = 6{\cdot}5810$ A. at 27°C.

A layer of rubidium chloride, deposited on the surface of a crystal of thallous chloride at −190°C., again has a cæsium chloride structure, with $a = 3{\cdot}742$ A. and density = 3·807 g./c.c.[40] On warming to 20°C., a transition occurs to another form of rubidium chloride having the sodium chloride lattice, although the value of *a* (6·53 A.) and the density (2·79 g./c.c.) are not the same as in the normal lattice. Rubidium chloride also forms oriented overgrowths on bismuth[41] and on potassium chloride and lead sulphide,[42] but it does not readily do so on sodium chloride.[43]

The root mean square amplitudes of vibration of both Rb^+ and Cl^- ions in the lattice at 290°K. were calculated to be 0·26 A.[44,45] from *X*-ray measurements.[46] These vibrations have also been treated theoretically.[44,47] The *X*-ray absorption spectra of rubidium in rubidium chloride[48] have been interpreted[49,50] in terms of the presence of exciton levels in the lattice.

The chlorine *K*-valence spectrum ($3p$–$1s$ transition) has been observed in the second order at a wave-length of about 9 A.[51]

The refractive index of a prism of rubidium chloride has been measured directly over the range 2000 to 6000 A.,[52] and Radhakrishnan[53] has given the following formula for the refractive index:

$$n^2 = 1{\cdot}4752 + [0{\cdot}55511\lambda^2/(\lambda^2 - 0{\cdot}019044)] + [0{\cdot}15241\lambda^2/(\lambda^2 - 0{\cdot}027556)] - 0{\cdot}0004\lambda^2]$$

The refractive index at 25°C. has also been given as $n_D^{25} = 1{\cdot}4937$.[32] In the infra-red, rubidium chloride shows a residual ray (representing a maximum of reflecting power), at 74 μ, close to the value calculated theoretically.[55] The calculated value of 47 μ for the wave-length of maximum transmission[55] is also close to the observed value.[56] At temperatures near the melting point, the maximum emissive power occurs at a wave-length of 4·8 μ, with two secondary maxima at 3·6 μ and 2·6 μ.[57] The nuclear magnetic resonance absorption of the ^{87}Rb isotope in the solid lattice is centred at a magnetic field which is 87 p.p.m. lower than the value found for the saturated aqueous solution of the salt.[58] This shift of the resonance is said to indicate the presence of partial covalent bonding in the solid. The diamagnetic susceptibility of the solid is $-46{\cdot}4 \times 10^{-6}$ c.g.s. units/mole,[59] the contributions of the Rb^+ and Cl^- ions being -22×10^{-6} and $-24{\cdot}2 \times 10^{-6}$ respectively.

The dielectric constant is 4·95 e.s.u.[23] although the value 4·68 has been given for a wave-length of 1800 metres at 18°C.[60] Skavani[61] has made a theoretical calculation of the dielectric constant. The dielectric strength, found[62] to be 0·8 mV./cm., has been interpreted theoretically[63] in terms of the lattice constants and ionic radii. Calculations also suggest that electric breakdown in the solid corresponds to a dissociation into ions[64] and that the dielectric strength should depend on the mechanical strength of the crystal.[65] The work of polarisation required to remove two adjacent ions ($Rb^+ Cl^-$) from the lattice has been calculated as ∼1·2 e.V./mole,[66] and that required to remove one ion as 4·53 e.V./mole for Cl^- and 4·27 e.V./mole for Rb^+.[67]

Kewzien[68] studied the transmission, through a thin layer of rubidium chloride, of electrons with kinetic energies in the range 0–12 e.V. The crystal was transparent to electrons with energies below 1 e.V., but those of increasingly higher energies were scattered more and transmitted less and less, except for two energy regions of selective transmission. Measurements of the conductivity between −180°C. and the melting point showed that the current obeys Ohm's law.[69] Earlier studies of the photoelectric effect[70] were extended by Pohl[71] who found that between −230 and 20°C. the temperature coefficient of the conductivity was positive and of the same order of magnitude as in metals.

In common with the other alkali halides, imperfections can be produced in the rubidium chloride lattice, either by the addition of one constituent in excess or of a foreign substance,[72] or by irradiation with high energy radiation such as ultra-violet light[73] or X-rays.[74] Certain imperfections such as lattice vacancies give rise to new absorbtion bands, having wave-length maxima related to the lattice dimensions.[67,75,76] Rubidium chloride which has been irradiated by X-rays has an anomalous dielectric constant at low (∼1000 c.p.s.) frequencies.[77] A review of the theory of one type of imperfection in alkali halides, the colour centres, is given by Gourary and Adrian[78] and there is another recent review of colour centres in alkali halides by Simons and Doyle.[79]

Molten Rubidium chloride.

Earlier measurements by Klemm of the conductivity[80] and density[81] of molten alkali halides have been extended by Yaffe and van Artsdalen.[17] They give the formula $\rho = 2{\cdot}8799 - 8{\cdot}832 \times 10^{-4}t$ for the density (g./c.c.) of the liquid over the temperature range 722° to 925°C. The standard deviation for the density values is 0·0002. For the specific conductance in ohms.$^{-1}$cm.$^{-1}$ over the range 730° to 935°C. they give the formula $K = -1{\cdot}809_7 + 0{\cdot}00617_6 t - 2{\cdot}198_5 \times 10^{-6}t^2$. The standard deviation for K is 0·002. For the conduction process, the heat of activation increases from ∼4·7 kg.-cal./mole at 725°C. to ∼4·3 kg.-cal./mole at 925°C. At 825°C., they calculate the corresponding entropy of activation to be ∼6·2 e.V. An earlier value for the entropy of activation of ionic migration in the melt was 2·830 kg.-cal./mole.[82] The surface tension of molten rubidium chloride was found to be 83 and 66 dynes/

cm. at 900 and 1100°C. respectively,[83] and 96 dynes/cm. at 750°C.[84]

Gaseous rubidium chloride.

Rubidium chloride is said to be appreciably volatile at about 600–700°C.[85] At 600°C. in a stream of water vapour (6 litres/hr.) it loses weight at a rate of about 0·27% per hr.; the residue and condensate are both unchanged chloride. It is less volatile in air or in hydrogen chloride. At 800°C. in air it is less volatile than cæsium chloride,[86] and in a vacuum at 440°C. the difference is sufficient to allow the chlorides to be separated by sublimation.[7]

The heat of sublimation is given as 46·4 kg.-cal./mole at ~600°C. by Treadwell and Werner,[87] 50·9 ± 0·9 kg.-cal. at 0°C. by Niwa[88] and 51·3 ± 2 kg.-cal. at 0°K. by Mayer and Wintner.[89] The latter authors give the formula $\Delta H(\text{vap.}T) = 4{\cdot}5738A - 3RT$ for the heat of vaporisation at temperature T°K., where $A = 11676$ for the crystal (giving the heat of sublimation) and $A = 10307$ for the molten salt above 988°K., (giving the heat of evaporation). Reis[90] calculates theoretically that the heat of sublimation is 50 kg.-cal./mole.

For the change of vapour pressure with temperature, Treadwell and Werner[87] give

$$\log_{10}p(\text{mm. Hg}) = \frac{-10{,}200}{T} + 9{\cdot}643$$

and Mayer and Wintner[89] give

$$\log_{10}p(\text{mm. Hg}) = \frac{-A}{T} - 3\log_{10}\left(\frac{T}{1000}\right) + C$$

where A has the values given above and $C = 11{\cdot}157$ for the crystal and $9{\cdot}772$ for the liquid; in both cases the temperature is in °K.

By means of mass spectroscopic analysis, Ionov[91] found dimeric molecules in alkali halide vapour. Miller and Kusch[92] studied the velocity distribution of alkali halide molecules escaping from a hole in a hot oven and found that rubidium chloride vapour consists of dimers and monomers in the ratio 0·088/1. They found also that the energy of dissociation of a dimer into two monomers is 48·1 kg.-cal./mole. Rice and Klemperer[93] were unable to detect any infra-red absorption lines from dimers in the vapour, indicating that dimers were present, if at all, to the extent of less than 15%. They later suggested[94] that the maximum proportion of dimers was considerably smaller than 15%, since the value for the entropy (and other thermodynamic functions) of gaseous rubidium chloride, calculated on the assumption of a 100% monomeric vapour, agrees fairly well with the experimental value. More recently, Berkowitz and Chupka[95] extended Ionov's work, and following his technique of mass spectroscopy to analyse the ions produced by electron impact on the vapour, found that dimers were present in the ratio 0·127/1 relative to monomers, in agreement with Miller and Kusch.

Srivata[96] studied the thermal dissociation of rubidium chloride vapour at 1350–1550°C. and calculated 114·7 kg.-cal./mole for the heat of dissociation into the separate ions in the vapour phase. Mayer and Wintner[89] had calculated 109·4 kg.-cal. at 0°K. for the energy of this same dissociation, and 160·7 kg.-cal./mole at 0°K. for the energy of the process: $\text{RbCl (cryst.)} \rightarrow \text{Rb}^+ \text{(gas)} + \text{Cl}^- \text{(gas)}$. They also calculated the energies (kg.-cal./mole at 0°K.) for the processes: RbCl (cryst.) → RbCl (gas), = 51·3; RbCl (cryst) → Rb (gas) + Cl (gas), = 152·8; and RbCl (gas) → Rb (gas) + Cl (gas) = 101·5.

The values calculated by Rice and Klemperer for some thermodynamic functions of rubidium chloride in the gas phase[94] are shown in Table I.

Their calculated value for the entropy at 298·16°K. is 59·852 g.-cal. $\text{deg.}^{-1}\text{mol.}^{-1}$, compared with the experimental value of 58·9 ± 2. Some of their values may be slightly in error since they assumed the vapour to be

TABLE I.- THERMODYNAMIC FUNCTIONS FOR GASEOUS RUBIDIUM CHLORIDE

Function	Temperature, °K.							
	298·16	400	600	800	1000	1250	1500	2000
$\frac{-(G_0-H_0^\circ)}{RT}$	26·062	27·271	28·983	30·225	31·200	32·186	32·995	34·290
$\frac{S^\circ}{R}$	30·123	31·434	33·262	34·572	35·593	36·622	37·464	38·809
$\frac{H-H_0^\circ}{RT}$	4·061	4·163	4·280	4·348	4·393	4·436	4·468	4·519

monomeric. Some of the earlier calculated values of the thermodynamic quantities[87,89,97] may also contain more serious errors, since the calculation of the entropy involves the internuclear distance and the fundamental vibration frequency of the rubidium chloride molecule in the gas, and the earlier values of 2·89 A. for the distance and 253 cm.$^{-1}$ for the frequency have now been superseded. Rice and Klemperer find the frequency to be 228 ± 6 cm.$^{-1}$,[93] and Trishka and Braunstein find the distance to be r_e = 2·78760 ± 0·00006 A.[98] The earlier determination of the distance was made[99] by electron diffraction on the vapour and the error may have arisen through failure to allow for the presence of dimers.[100]

Rittner[101] calculated a value of 10·07 debye for the dipole moment of gaseous rubidium chloride, and Altshuller[102] calculated the difference between the moments of $Rb^{35}Cl$ and $Rb^{37}Cl$ to be 1·1 × 10^{-4} debye.

Ionov[103,104] used the mass spectrometer to study the formation of negative ions when alkali halides are ionised at a heated tungsten surface, and from the results for rubidium and potassium chloride, he derived the value 3·7 e.V. for the electron affinity of chlorine. He also found[105,106] that a low pressure discharge in the vapour produces the negative ions Cl^-, Cl_2^-, Rb^-, $RbCl^-$ and $RbCl_2^-$ together with the positive ions Rb^+, $RbCl^+$ and Rb_2Cl^+. The amounts of Rb^-, Cl_2^- and $RbCl^-$ are similar and about 1% of the amount of Cl^-.[107] Like other alkali halides, rubidium chloride introduced into flames produces ions[108] which under some conditions seem to be mainly Rb^+,[109] the Cl^- being removed as HCl. Mandelsh'tam[110] calculated the degree of dissociation of rubidium chloride in flames at ~2000°C.; in some types of flame the salt is 85% dissociated into ions.

Aqueous solutions of rubidium chloride

The integral heat of solution of rubidium chloride at 18°C. is 4·235 kg.-cal./mole in water and 4·835 kg.-cal./mole in deuterium oxide.[111] The total heat of hydration of the salt has been calculated as 153 kg.-cal./mole,[112] and the sum of the standard free energies of the ions as 146·6 kg.-cal./mole.[113] The effective radii of the Rb^+ and Cl^- ions in solution are estimated as 1·37 and 2·37 A. respectively.[114] The minimum hydration of the Rb^+ ion in solutions is found to be $4H_2O$ from measurements of the dielectric properties at microwave frequencies;[115] the hydration has also been estimated from measurements of vapour pressure[116] and ultrasonic absorption.[117] Gehlen and Dieter[118] calculated that the solubility should increase from 46·2% by weight at 25°C. under normal pressure to 60·8% under 10,000 atm. The surface tensions of solutions containing 2·00, 3·30 and 5·00 moles/kg. of solvent are 75·2, 76·8 and 79·2 dynes/cm. respectively.[216]

The diffusion rate is 0·542, 0·549, 0·637 and 0·761 in 4 N, 2 N, 0·5 N, and 0·1 N solutions respectively.[119] The differential diffusion coefficient at 25°C. is found by conductometric methods to vary from 2·012 × 10^{-5} cm.^{2}sec.$^{-1}$ in 0·00176 M. solutions to 1·969 × 10^{-5} in 0·01110 M. solutions,[120] the limiting value at infinite dilution being 2·057 × 10^{-5}. From these measurements the mean ionic activity coefficients in dilute solutions were determined;[121] some values at 25°C. are 0·975, 0·966, 0·951, 0·928 and 0·901 for concentrations of 0·5, 1, 2, 5 and 10 millimoles/litre.[122] For higher concentrations, the values in Table II have been given for 25°C. by Robinson and Stokes.[123]

TABLE II.- MEAN IONIC ACTIVITY COEFFICIENTS OF RUBIDIUM CHLORIDE IN AQUEOUS SOLUTION AT 25°C.

molality m	mean ionic activity coeff. $\gamma\pm$	molality m	mean ionic activity coeff. $\gamma\pm$	molality m	mean ionic activity coeff. $\gamma\pm$
0·1	0·764	0·8	0·599	2·0	0·546
0·2	0·709	0·9	0·590	2·5	0·539
0·3	0·675	1·0	0·583	3·0	0·536
0·4	0·652	1·2	0·572	3·5	0·536
0·5	0·634	1·4	0·563	4·0	0·538
0·6	0·620	1·6	0·556	4·5	0·541
0·7	0·608	1·8	0·551	5·0	0·546

These values are in close agreement with those given by Harned and Owen,[124] who also tabulate other thermodynamic properties of the aqueous solution. The activity coefficient of the water in these solutions has been calculated.[125]

The refractivity[126] and the Faraday effect[127,128] in the solutions have been studied, and the dielectric properties measured at microwave frequencies.[115] From these measurements the static dielectric constants for 0·5, 1, 1·5 and 2 N. solutions at 25°C. are found to be 73·5, 68·5, 63·5 and 58·5 respectively. The dielectric constant can be expressed as $\epsilon = \epsilon_w + 2\bar{\delta}c$ where ϵ_w is the dielectric constant for water (=78·5 at 25°C.), c is the concentration in moles/litre, and $\bar{\delta} = -5$ for RbCl. The contribution to $2\bar{\delta}$ from Rb^+ is −7 ± 1 and that from Cl^- is −3 ± 1.

The equivalent conductivity of the solutions of concentrations 0·5, 1, 1·5 and 2 N are given[115] as 125·5, 114·7, 107·5 and 104·5 $\text{ohm}^{-1}\text{cm.}^{-2}$ respectively. The conductivity can be calculated satisfactorily by theory for solutions up to 1 N.[129] The equivalent conductivity passes through a maximum with increasing pressure,[130] an effect which indicates that there must be an appreciable change in the (effective) diameter of the ions at high pressures. Electrolysis of the solutions between platinum electrodes gives rubidium chlorate which precipitates out, in contrast to other alkali metals the chlorates of which stay in solution and are oxidised further to perchlorates:[131] after passing 150 amp. hours at 60°C., 99·8% of the chloride in a rubidium solution was converted to chlorate.

Non-aqueous solutions of rubidium chloride

In concentrated hydrochloric acid the solubility of rubidium chloride is[6] 1·56 moles/litre at 20°C. The equivalent conductivity in liquid hydrogen cyanide at 18°C. is given by the equation $\Lambda = 363{\cdot}2 - 195\sqrt{c}$ where c is the concentration in moles/litre.[132] The mobilities of the Rb^+ and Cl^- ions under these conditions are 153·2 and 210, respectively, greater than the corresponding values of 67 and 65 in water at the same temperature. The solubility in liquid ammonia at 25°C. is 0·22 ± 0·03 g. of the salt in 100 g.[133] In liquid sulphur dioxide, the solubility is 0·0272 moles/1000 g. of solvent at 0°C.[133] and 0·402 g./100 g. solution at 25 ± 0·02°C.[134] In this solvent, rubidium chloride is an effective catalyst for the exchange of sulphur between the solvent and thionyl chloride[135] or thionyl bromide.[136] The solubility in anhydrous phosphorus oxychloride at 20°C. is 1·26 g./litre, the specific conductivity of the saturated solution being $1{\cdot}1 \times 10^{-4}\,\text{ohm}^{-1}\text{cm.}^{-1}$.[137] The conductivity has also been measured in solutions in fused antimony trichloride,[138] where the mobility of the Rb^+ ion is only 22·5.[139] In iodine monochloride, rubidium chloride acts as a base.[140] Cryoscopic[141] and electrochemical[142] studies indicate that when the salt dissolves with aluminium tribromide in aromatic solvents, a 1:1 complex is formed, $(AlBr_3Cl)Rb \rightleftharpoons (AlBr_3Cl)^-Rb^+$. In benzene solution, the dipole moment of $RbCl,Al_2Br_6$ was found to be 10·5 debye.[143,144] Electrolysis of acetic acid solutions[145] gives rubidium acetate. The solubility of rubidium chloride in ethanol at 20°C. is 0·0023 moles/litre:[8] in methanol at 18°C., the solubility (L^{18}) is 1·30 g./100 g. solvent, corresponding to a concentration in moles/litre of $c^{18} = 8{\cdot}50 \times 10^{-2}$; the density ($d^{18}$) of the saturated solution is 0·800 g./c.c. The corresponding values for methanol at 25°C. are $L^{25} = 1{\cdot}34$, $c^{25} = 8{\cdot}71 \times 10^{-2}$ and $d^{25} = 0{\cdot}797$.[146] In acetonitrile, $L^{18} = 3{\cdot}4 \times 10^{-3}$, $c^{18} = 2{\cdot}2 \times 10^{-4}$, $d^{18} = 0{\cdot}783$; and $L^{25} = 3{\cdot}6 \times 10^{-3}$, $c^{25} = 2{\cdot}3 \times 10^{-4}$, $d^{25} = 0{\cdot}777$. In formic acid the solubility is much greater; $L^{18} = 60{\cdot}2$, $c^{18} = 5{\cdot}01$, $d^{18} = 1{\cdot}611$ and $L^{25} = 56{\cdot}9$, $c^{25} = 4{\cdot}66$, $d^{25} = 1{\cdot}553$. In acetonitrile,[147] rubidium chloride will undergo a reversible one-electron polarographic reduction. The salt is practically insoluble in acetone.[148] From measurements of the depression of the freezing point in formamide,[149] the activity coefficients in this solvent are found to be 0·929, 0·883 and 0·854 at concentrations 0·02, 0·1 and 0·4 *m*. respectively.

Mixed crystals and double salts of rubidium chloride

(*a*) Systems with other rubidium salts.

The critical solution temperature of solid solutions of rubidium chloride and rubidium bromide has been estimated as 173·2°K.[150] Values of the unit cell dimension *a* for mixtures of rubidium chloride and bromide containing 0, 16, 34, 50, 78 and 100% of rubidium bromide are found by *X*-ray diffraction to be 6·591, 6·630, 6·691, 6·736, 6·827 and 6·895 A. respectively.[38] The heat of formation of this solid solution has been calculated theoretically.[151] A study of the system $RbCl–RbBr–H_2O$ shows that the mixed crystals can be prepared from aqueous solutions.[152] The system RbCl–RbF has a eutectic at 545°C. with 53 mole-% of rubidium chloride.[153] The phase diagram for the system $RbCl–RbNO_3$ shows the existence of two complexes, one containing 10·4 mole-% $RbNO_3$, at 340°C., the other containing 24 mole-% $RbNO_3$, at 394°C.[154] The system $RbCl–RbVO_3$ shows a simple eutectic.[155]

(*b*) Systems with potassium chloride.

Rubidium and potassium chlorides form a continuous range of solid solutions without a minimum or maximum in the melting point.[26,156] A rough phase diagram for the molten salts is given by Tamman and Krings.[157] The melting points of the solid solutions containing 0, 0·2, 0·4 and 0·6 mole-% of rubidium chloride are given as approximately 781, 745, 727 and 718°C. respectively. These results indicate that the melting points of mixtures rich in chloride are not very different from the melting point of the pure salt, but the value of ~713°C. given for the pure salt is rather low (see page 2197). The solid solutions can also be prepared by crystallisation from aqueous solution.[158,159] When prepared from aqueous solutions, the proportion of rubidium in the solid is always less than that in solution, as was shown by Tamman and Krings[157] and in particular by d'Ans and Busch[158] who give the data shown in Table III. Although there is some evidence[157] that mixed crystals grown from solution may not be homogeneous, Hovi[159] found by *X*-ray diffraction studies that very homogeneous mixed crystals could be produced by crystallization under controlled conditions. The mixed crystals can also be obtained by saturating with hydrogen chloride an ethanolic solution of the two salts.[160] The average error involved in analysing mixtures

TABLE III.- COMPOSITION OF SOLID SOLUTIONS OF RUBIDIUM AND POTASSIUM CHLORIDES FORMED BY CRYSTALLISATION FROM AQUEOUS SOLUTION

In 1000 moles H_2O		Mole-% RbCl	
Rb_2Cl_2	K_2Cl_2	in solution	in solid
70·1	0	100	100
59·3	10·4	85·1	84·5
51·0	17·5	74·5	58·2
41·2	22·5	64·7	32·7
31·0	28·0	52·6	15·5
19·2	33·5	36·5	7·4
10·0	37·6	20·8	2·4
0	43·5	0	0

in the range 36–46 mole-% KCl is said to be 0·2 mole-%.[161] The heat of formation of the 50% solid solution was found to be 203 g.-cal./mole.[162] Several calculations of the heat of formation have been made.[163,164] Fineman[165] shows that a simple equation, originally derived for liquid solutions by Hildebrand, gives a theoretical value (277 g.-cal./mole) which is in better agreement with the experimental value than are values calculated on the basis of the Born–Mayer theory by Wallace[166] or the older Born theory by Tobolsky.[167] Heats of solution of crystals grown from aqueous solution were found to be about 1 to 4% greater than for crystals of the same composition grown from the melt;[157] for the 50% solution the values were 48 and 46 g.-cal./g. respectively. The free energy of formation has been calculated, and so has a value of −70°C. for the critical solution temperature.[168]

An *X*-ray study of the 50% solid solution showed that the mean square displacement of the chloride ion is about 2×10^{-18} cm.^{2}. This value is considerably greater than the corresponding displacement in the pure component salts, indicating permanent displacements from regular lattice points.[46]

The dielectric strength of the solid solution increases with the melting point but passes through a maximum with the mixture melting at 750°C.[169] A theoretical treatment of the dielectric breakdown has been given,[170] and refractive indices of the mixed crystals have been determined.[171] The mixed crystals show only one maximum in the reflected infra-red radiation,[172] whose wave-length lies between the $\lambda_{max.}$ of the pure salts and varies linearly with concentration. The presence of lattice defects[173] or small amounts of substances such as hydrogen ions[174] or thallous chloride[175] gives rise to new absorption bands or phosphorescence spectra,[174] similar to those of defect lattices of the single components.

(*c*) Systems with other chlorides of the types MCl and MCl_2.

Rubidium chloride and lithium chloride form a double salt with an incongruent melting point,[25] and the system AgCl–RbCl shows a eutectic.[176] Thermosensitive resistance elements can be made[177] using eutectic mixtures having compositions as follows where T_0 is the optimum temperature for each particular mixture:- RbCl 40% + CuCl 60%, T_0 = 150°C.; RbCl 36% + AgCl 64%, T_0 = 270°C.; RbCl 80% + LiCl 20% (T_0 = 290°C.).

With magnesium chloride, the compounds $RbMgCl_3$ and Rb_2MgCl_4 are formed;[178] with strontium chloride[25] the phase $RbCl,SrCl_2$ has a congruent melting point at 674°C. and $RbCl,2SrCl_2$, a congruent melting point at 646°C. The only mixed phase formed with $BaCl_2$ is $2RbCl,BaCl_2$, with a congruent melting point at 649°C.,[25] also reported as at 650°C.[153] With calcium chloride there are two eutectics, at 17 mole-% RbCl (696°C.) and 78 mole-% RbCl (630°C.), and a compound $RbCaCl_3$ is formed with a melting point of 930°C.[179] Chu and Egan,[180] who reproduce the phase diagram for this system, have recently used these data to calculate the free energy of mixing and other thermodynamic properties for the $RbCl-CaCl_2$ system. For the system with cadmium chloride, Hofman[25] found the mixed phases $4RbCl,CdCl_2$ (incongruent melting point at 476°C.), $3RbCl,2CdCl_2$ (incongruent melting point at 451°C.) and $RbCl,CdCl_2$ (congruent melting point at 495°C.); whereas Dergunov[181] found only the compounds $RbCdCl_3$ (m.p. 500°C.) and Rb_2CdCl_4 (m.p. 448°C.). With manganese chloride[182] two compounds are formed, $RbCl,MnCl_2$, m.p. 552°C., and $2RbCl,MnCl_2$, m.p. 466°C. There are three eutectics at 460°, 454° and 436°C. corresponding respectively to 31, 67 and 71 mole-% of rubidium chloride.

(*d*) More complex systems with other chlorides.

The ternary systems RbCl-LiCl-KCl and RbCl-KCl-CsCl[26] and also $RbCl-CsCl-CdCl_2$[181] have been studied. The system $RbCl-NaCl-CaCl_2$[183] has two eutectics, one with a melting point of 500°C. and composition 2·5, 45 and 52·5% respectively; the other with a melting point of 505°C. and composition 56·0, 32·8 and 11·2%. In the system $RbCl-LiCl-H_2O$ the double salts $RbCl,2LiCl,4H_2O$ and $3RbCl,LiCl,2H_2O$ are found at both 25°C. and 40°C.[184,185] The system $KCl-RbCl-MgCl_2-H_2O$ has been studied at 25°C.[158,186] and at 100°C.;[187] and $RbCl-KCl-NH_4Cl-H_2O$ at 25°C.[188]

(*e*) Systems with other halides.

The unit cell dimensions and the molecular weights are almost equal for rubidium chloride and potassium bromide, and they form solid solutions very easily. *X*-Ray[189] and refractive index[190] studies show that when any mixture of the two salts is melted, one solid solution is formed which contains all the ions in the original mixture. Rubidium chloride diffuses slowly into a crystal of potassium bromide when the two are heated together at 400–600°C.[191] Meissner and Pick[192] have measured the absorption bands of the *F*-centres in imperfect lattices of this solid solution of various compositions.

There is one simple eutectic in the system RbCl-AgI,[193] but there are three in $RbCl-NaNO_3$.[27] Other systems which have been measured are $RbCl-BaF_2$,[153] $RbCl-Na_2SO_4$ and $RbCl-K_2SO_4$[194] and $[Mg, Ca, Co]SO_4-[Na, K, Rb]Cl$.[195] A small amount of rubidium chloride lowers the temperature of miscibility of other salt systems.[196,197] Diogenov's classification of reciprocal salt systems[198] includes some of those mentioned above. In boric oxide glasses, rubidium chloride forms colloidal solutions.[199,200]

Miscellaneous reactions

If rubidium chloride is irradiated in an atomic pile, some of the chloride nuclei are converted to radioactive ^{35}S, and 50% of this active sulphur can be separated as $H_2^{35}S$ by extraction with hydrochloric acid containing a little hydrogen sulphide as carrier. The separation from radioactive rubidium is very effective. The advantage of using rubidium rather than potassium chloride is that with the latter it is not so easy to get a good separation of the active sulphur.[201]

Rubidium chloride and lithium hydride[202] react to give rubidium metal and hydrogen. The hydrolysis by water vapour to give hydrogen chloride and the hydroxide is said to be more effective with the molten salt than with the solid;[203] but it has also been suggested[85,86] that the chloride can sublime unchanged in a stream of water vapour at 600°C. An unstable compound is formed with vanadium tetrachloride.[204] Rubidium chloride is completely converted to the borate on heating for ten minutes at 400°C. with eight parts of boric acid.[205]

Rubidium chloride inhibits the combustion of gaseous hydrocarbons, probably owing to a recombination of hydrogen atoms and hydroxyl radicals on the crystal surfaces.[206,207] The streaming potentials of dilute solutions on the salt have been studied,[208] and so have its effects on the electrical double layer at a mercury surface[209] and on the potentials across protoplasm in cells.[210] The diffusion coefficient in gelatin gels is given as 1·13 × 10^{-5} c.g.s. units.[211] The salt is more effective than potassium chloride in coagulating sols of arsenic trisulphide[212,213] or of graphitic oxide.[214] Measurements are given of the effects of rubidium chloride, and other alkali halides, on the surface absorption[215] and spreading pressure[216] of colloidal electrolytes on water surfaces, on the cataphoretic activity of glass beads,[217] and on the adhesion of solid particles.[218] Rubidium chloride can partly replace potassium chloride in the binding[219] or activation[220] of certain enzymes. Comparative studies of rubidium chloride and other alkali halides have also been made in several biological systems, for example, with respect to their concentration in blood[221,222] and their effects on sugar exchange,[223] on the fragility of human red cells,[224] on the activity of auxin,[225] on diuresis[226] and oxaluria,[227] and also regarding their toxicity to the central nervous system[228] and their effects on the growth of bacteria.[229,230,231]

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SECTION LXX

RUBIDIUM BROMIDE

By N. R. W. BENWELL

Physical Properties

X-Ray study of the crystal structure of compounds formed by equal numbers of each of two oppositely charged ions which are cubic according to the theory of Lewis, Born and Landé, and Langmuir shows that rubidium bromide is an elementary simple cube of side 3·465 A.[1] *X*-Ray measurements by other workers give the length of the side of the unit cube of rubidium bromide as 6·868 A., the effect of small amounts of isomorphous impurities (<1%) on the length of the side being negligible.[2] Application of the Thomas–Fermi method gives (when polarization forces are neglected) a value of 3·8 A. for the lattice constant (experimental – 3·42 A.)[3] Consideration of the lattice energy of rubidium bromide shows that the NaCl structure leads to the most stable configuration.[4] The electrically measured ionic emission through an orifice in an equilibrium chamber containing rubidium bromide vapour, combined with known thermal data, gives a lattice energy of 151·3 kg.-cal. at 0°K., the probable error being 3 kg.-cal. This value is in good agreement with that derived from lattice theory.[5]

Molar refraction and ion distance determinations for alkali metal halides having a noble gas shell such as rubidium bromide lead to ion radii and polarizability values in good agreement with values determined in other ways and thus indicate that univalent ions of the same shell structure do not deform themselves in such lattices. The ratio of the radii in such lattices is always approximately 0·73. From ion radius, ion refraction and polarizability data are in good agreement with similar values calculated theoretically or empirically. For rubidium bromide, ion distance = 3·439 A., molar refraction = 16·5 cm.^{3} (15·8); ion radii = 1·46 A. for Rb^+, 1·98 A. for Br^- (1·49, 1·96; 1·48, 1·95); ion polarizability, = 1·31 A.^{3} for Rb^+, 5·19 A.^{3} for Br^- (1·47, 4·22). Figures in brackets are theoretically and empirically determined values.[6]

The root mean square amplitude of atomic vibration of rubidium bromide at 293°K. = 0·29 (Lonsdale).[7] The frequencies and anharmonicities of the lattice oscillations of rubidium bromide, *i.e.* the oscillations of the interpenetrating lattice of the rubidium and bromine ions with respect to one another, have been calculated on the basis of the Born model. The calculated value of the frequency of lattice oscillation, $2{\cdot}6 \times 10^{-12}$, is in exact agreement with the observed value (Krishnan and Roy). The anharmonicity of the lattice oscillation, unlike its frequency, varies with the direction of the oscillation from a large positive value along [111] to a small negative value along [100].[8]

The intensity of orbital interaction of salts with ions of elements of atomic number one above or below the rare gases (*i.e.* with 6*p* electrons) is calculated from the equation $T = F_0\sqrt{N}$ where T = m.p.(°K.); N = number of orbital contacts. For rubidium bromide, where $N = 12$, $F_0 = 273$.[9]

A new region of anomalous electrical response is observed at low frequencies in ionic crystals of a number of univalent halides including rubidium bromide. The effect is attributed to a jumping of the positive ions to vacant lattice sites under the influence of the applied field. This jumping is observed as a relaxation process producing a change in the dielectric constant which is small and frequently within the limits of error of measurement, and an associated peak in the dielectric-loss tangent which is readily measurable. From the magnitude of the peak ($\tan \delta_{\text{max.}}$) and its position on the frequency or temperature scales, is calculated the number of lattice defects in the crystal and the activation energy for diffusion, U, of the positive ion. A knowledge of U leads to separation of the activation energy for conduction, $(\frac{W}{2}) + U$ into its components and thus, W, the activation energy for hole formation is determined. For rubidium bromide at 57°C. and a frequency of 10^3 cycles/sec., $U = 0{\cdot}58$ e.V., $\frac{W}{2} + U = 2{\cdot}03$ e.V. and $W = 2{\cdot}9$ e.V. The time constant for the natural frequency of lattice vibration[10] $= 0{\cdot}38 \text{sec.} \times 10^{12}$.

Microscopic observation of the crystal growth of rubidium bromide on grease-free potassium chloride, rock salt and Joplin galena shows that the crystals are oriented on potassium chloride and galena but not on rock salt. Ease of orientation appears to depend on the dissymmetry as measured by the ratio of anion to cation radius.[11] When grown from solution on oriented silver films, rubidium bromide has the CsCl-type structure with a lattice constant of 4·06 A. When grown in vacuo from the vapour, rubidium bromide has its normal NaCl-type structure with a [111] fibre orientation. When this film is dissolved by exposure to moist air and recrystallised by drying, the rubidium bromide assumes the CsCl structure oriented with the crystallographic axes parallel to those of the silver.[12]

Large single crystals of rubidium bromide have been grown by raising a seed crystal from a melt which is maintained slightly above the melting point of the salt.[13] Colouration can be produced in rubidium bromide crystals by several hours' exposure to "intense X-rays." The colour fades logarithmically with exposure to daylight and fading is also induced by radiation from electric light.[14]

Measurements of the specific heats, C_p and C_v, of rubidium bromide by vacuum calorimeter show a rise of specific heat at constant pressure from 0·31 at 10·5°K. to 6·24 at 272·7°K. and for the specific heat at constant volume from 1·52 at 22·2°K. to 5·94 at 176°K. In this temperature range the characteristic Debye temperature, θ, varies between 120 and 135, thus deviating from the prediction of the Debye theory that θ is constant.[15]

The electrical conductivity of rubidium bromide at its melting point, 681°C., is $3{\cdot}5 \times 10^5$ amp. volt.$^{-1}$cm.$^{-1}$ Ohm's law is generally valid, but the conductance depends on temperature, in agreement with van't Hoff's equation.[16]

The following details of compressibility of rubidium bromide have been determined by Bridgman's method: (1) Compressibility at 30°C., $7{\cdot}94 \times 10^{-12}$; (2) Compressibility at absolute zero by extrapolation, $6{\cdot}5 \times 10^{-12}$; (3) Change of compressibility with pressure, independent of temperature between 30°C. and 75°C., 35×10^{-12}. As would be expected, the change of compressibility with temperature is related to the thermal expansion in such a way that an increase in temperature and decrease in pressure have the same effect on both volume and compressibility.[17]

A further expression for compressibility is given by Szigeti:

$$\frac{1}{\kappa} = \frac{R^2}{3v} \cdot \frac{\epsilon + 2}{n^2 + 2} \cdot m\omega_t^2$$

where κ = compressibility; ω_t = absorption frequency; R = nearest neighbour distance; v = volume occupied by an ion pair; ϵ = dielectric constant; n = optical refractive index; m = reduced mass of the ion pair. The following values have been obtained[18] for the equation applied to rubidium bromide:

Type		NaCl
R	(10^{-8}cm.)	3·42
$R^2/_{30}$	(10^6cm.)	4·88
ϵ		5
n^2		2·33
$m\omega_t^2$	(10^4dynes/cm.)	1·9
$\kappa_{\text{calc.}}$	(10^{-6}cm.^{2}/kg.)	6·84
$\kappa_{\text{obs.}}$		7·78
κ_c/κ_o		0·83

The cubic compressibility of rubidium bromide is given as 8·2 per megabar × 10^{-6} as derived from the semi-empirical formula $\beta = kV_m/U$ where β = compressibility; k = empirical constant; V_m = molecular volume; U = molecular heat of formation of the salt. This equation is considered more accurate than that derived by Born from consideration of the Bohr theory of atomic structure.[19] The compressions of rubidium bromide under 50,000 kg./sq.cm. at room temperature and at the temperature of solid carbon dioxide are 0·2848 and 0·2774 respectively. A transition occurs at 4,050–5,000 kg./sq.cm.[20]

Consideration of the anharmonic properties of a linear chain suggests that the dimensionless quantity $\alpha\gamma T$ is in general a measure of the anharmonicity of a lattice (α is the thermal expansion coefficient and γ is the Grüneisen parameter). Experimental evidence in the case of rubidium bromide and other alkali metal halides supports the supposition that the mean free path for lattice vibrations of a thermal insulator should, in the classical temperature region, be approximately $A_o/\alpha\gamma T$ where A_o is the lattice spacing.[21]

Recent calculations of the dielectric constant of rubidium bromide by various methods differing in the evaluation of the ionic polarizability have given values in satisfactory agreement with experimental data. The evaluation is based on the calculation of an elastic force coefficient, k, between opposed ions as the second derivative of the repulsion energy, from formulæ of this type: $k = 1{\cdot}16(n - 1)q^2/r_0^3$ where n = exponent of the repulsion energy law; q = charge of the ion; r_0 = nearest distance in the lattice.[22]

In investigating the mechanical stresses in dielectrics in electrical breakdown, if the breakdown potential of rubidium bromide is plotted as a function of the pressure developed in the dielectric crystal through the application of the electric field just before the breakdown, it has been found that with pressure increasing in a definite order the breakdown potential increases at first rapidly and then more slowly. This indicates that the weakening of the mechanical strength due to the high stress results in a lowering of breakdown potential. On the other hand, the stress increases with increasing lattice energy. A practical inference is that increased mechanical strength should result in an increased dielectric strength.[23] In further considering the electric breakdown of solid dielectrics, the same author assumed that breakdown takes place when energy accumulated by the electrons and transferred to the rubidium bromide lattice is sufficient to break the bond between the lattice points, but experimental data did not bear this out, indicating more nearly a linear relation between field strength and lattice energy and a dissociation of the lattice into ions and not into neutral atoms. The decrease of the time interval between electron collisions, with increasing electric field strength, holds only at sufficiently high field strengths, possibly when the kinetic energy of the electrons becomes comparable with the vibration energy of the lattice points.[24] The dielectric constant of rubidium bromide, expressed in terms of the close packing of the lattice and of the valence bond, is in good agreement with experimental data.

When the dielectric strengths of rubidium halides are plotted with respect to heats of formation of the solid and gaseous states, straight lines of positive slope are obtained.[25] The value of the dielectric strength of rubidium bromide is given[26] as 0·6m.V./cm.

Measurements of the density of molten rubidium bromide at several temperatures have shown that Mendelyeev's equation for the thermal expansion of "ordinary liquids" also holds for molten salts.[27] The degree of thermal dissociation of gaseous molecules of rubidium bromide at 2000°C. calculated[28] by an approximate equation for the equilibrium constant K_p, with values of the heat of formation taken from the literature, is 4×10^{-5}.

The heat of vaporisation of rubidium bromide has been determined[29] from the expression: $\lambda = -1{\cdot}985 \times 2{\cdot}303 \times [d\log P/d(1/T)]$ to be 39,970 g.-cal. The same author gives the boiling point as 1340°C. by calculation or extrapolation of vapour pressure data, and a critical temperature = 2500°K. Greater accuracy is claimed for these results than for those calculated by the Ramsay–Young rule. The vapour pressure curves of the alkali bromides at temperatures between the boiling point and 200–300°C. below the boiling point of the salt lie closer than those of the fluorides but are more widely spaced than those of the iodides.[30] For gaseous rubidium bromide, interatomic distance = 3·04 A , fundamental frequency = 210 cm.$^{-1}$ and entropy ($S_{298\cdot1}$) = 60·1 g.-cal./degree, the uncertainty being ± 0·3 e.V.[31] Investigation of the thermal dissociation of rubidium bromide vapour into ions in the temperature region 1350–1550°C. has given a value of 106·9 kg.-cal. for the heat of dissociation.[32] Using Knudsen's molecular effusion method, the vapour pressure of rubidium bromide was found to increase in the temperature range 856°–911°K. from 8·0 to $44{\cdot}4 \times 10^{-3}$ mm. and an average value of ΔH (vapour) at 900°K. was found to be 47·4 ± 2·0 kg.-cal. ΔH (vapour) at 0°K. = 51·2 ± 2·3 kg.-cal. For the crystal, fundamental frequency = 125·6 cm.$^{-1}$ and entropy (900°K.) = 39·9 ± 1·4 g.-cal./degree. For the gas, fundamental frequency = 198 cm.,$^{-1}$ entropy (900°K.) = 72·2 ± 0·5 g.-cal./degree and interatomic distance = $3{\cdot}06 \times 10^{-8}$ cm. In the equation: $\log_{10} P_{\text{mm.}} = -A/T - 3\log_{10}(T/1000) + C$ for RbBr (crystal), $A = 11514$, $C = 11{\cdot}156$; for RbBr (liquid), $A = 10224$, $C = 9{\cdot}805$. Melting point = 955°K. Energies, in kg.-cal. at 0°K., of the reactions are: $\text{RbBr}_{\text{crystal}} \rightarrow \text{RbBr}_{\text{gas}} = 51{\cdot}2$; $\text{RbBr}_{\text{crystal}} \rightarrow \text{Rb}^+_{\text{gas}} + \text{Br}^-_{\text{gas}} = 153{\cdot}5$; $\text{RbBr}_{\text{gas}} \rightarrow \text{Rb}^+_{\text{gas}} + \text{Br}^-_{\text{gas}} = 102{\cdot}3$; $\text{RbBr}_{\text{crystal}} \rightarrow \text{Rb}_{\text{gas}} + \text{Br}_{\text{gas}} = 141{\cdot}6$; $\text{RbBr}_{\text{gas}} \rightarrow \text{Rb}_{\text{gas}} + \text{Br}_{\text{gas}} = 90{\cdot}4$.[33]

Using the latest data on dispersion and absorption, a formula of the Drude form has been developed[34] for rubidium bromide: $n^2 = 1{\cdot}4500 + [0{\cdot}2000\lambda^2/(\lambda^2 - 0{\cdot}015129)] + [0{\cdot}3651\lambda^2/(\lambda^2 - 0{\cdot}022650)] + [0{\cdot}3224\lambda^2/(\lambda^2 - 0{\cdot}033124)]$.

The magnetic susceptibility of rubidium bromide, the sum of the atomic numbers of whose constituents differs by unity from that of krypton (Rb 37, Br 35, Kr 36) has been measured[35] and from the results has been deduced, by interpolation, the magnetic susceptibility of krypton. For rubidium bromide, susceptibility $K = -62{\cdot}9 \times 10^{-6}$ and on the assumptions that the constituent elements are in the ionic condition and that susceptibility is proportional to the square of the atomic number, for rubidium, $\kappa = -29{\cdot}9 \times 10^{-6}$ and for bromine, $\kappa = -33{\cdot}0 \times 10^{-6}$.

When the permanent electric moment of rubidium bromide in which the ions have a rare gas structure is calculated by Debye's formula, the results differ from experimental values, the difference being ascribed to deformation of the external electron shells. The moment varies regularly with the number of electrons in the molecule.[36]

Magnetic resonance shifts in the alkali metal halides have been determined, based on the work of Ramsay who has shown that chemical shifts result from precessional motions induced by the applied magnetic field in the electrons surrounding the nucleus. This precessional motion produces a small local field at the nucleus in opposition to the applied field and this local field will vary from molecule to molecule as a result of the variations in electronic structure. 100% ionic compounds have no chemical shifts and so the shielding change observed for rubidium bromide indicates that there is some covalent character in the crystalline bond. The chemical shift of the ^{87}Rb magnetic resonance: $\Delta\sigma = (H_s - H_r)/H_r \times 10^4$, where H_s and H_r are the magnetic fields necessary for resonance at a fixed frequency for the sample and reference respectively, is −1·29 for rubidium bromide, the reference being a saturated solution of rubidium chloride. The magnetic shielding of the alkali metals decreases from the fluoride to the iodide, while the ion in solution has the largest shielding of all. The smaller shifts of rubidium support the observation that the chemical shifts decrease with decreasing nuclear charge.[37]

The formation of negative ions in the process of surface ionization has been investigated[38] by directing a molecular beam of rubidium bromide against a heated tungsten filament. The ions are drawn off by means of an electric field and separated from electrons by means of a magnetic field. The negative current thus produced increases markedly with increasing temperature of the filament. A thermodynamic treatment, analogous to that followed in the deduction of Langmuir's equation, is applied to calculate the probability of a bromine atom evaporating from the filament as a negative ion and establishes a value for the electron affinity of bromine atoms of 3·64e.V.

Investigation of the heat effect, Q, of the exchange reaction between sodium thiocyanate and rubidium bromide (uni-univalent salts), when calculated as the algebraic sum of the four lattice energies, shows a discrepancy,[39] possibly due to an incorrect heat of formation for RbCNS of 56kg.-cal. (suggested, 50·4kg.-cal.). The equation for the reaction AX + BY $\rightarrow$ AY + BX: $Q = 512(a + x + b + y)(a - b)(y - x)/(a + x)(b + y)(a + y)(b + x)$ where a, b, x and y are the ionic radii of A^+, B^+, X^- and Y^- respectively, gives good agreement with experimental data for other exchange reactions involving univalent ions. For the reaction NaCNS + RbBr, Q (calculated) = 0·16, (experimental) = −6.

The migration of ions through crystals has been studied in the reactions of macrocrystals of potassium bromide and potassium chloride with fine powders of very pure rubidium chloride and rubidium bromide at 400–600°C. These show that all four species of ions are formed and that the rate of penetration increases with temperature.[40]

In the refractive index study of the solid solutions formed by the system RbCl + KBr $\rightleftharpoons$ RbBr + KCl, for some areas of the composition diagram, the results of X-ray diffraction analysis expected for a single ternary solid solution and for a co-existing pair of binary solutions cannot be distinguished from each other. In these areas, the refractive indices calculated for the two interpretations of the X-ray measurements differ considerably and thus indicate the correct interpretation. All observations are in accord with the view that one solid solution is formed which contains all of the four ion species for each mixture.[41] Ricci[42] believes the interpretation of the refractive index measurements to be inconsistent and some of the conclusions to be incorrect.

Table I[43] gives data for the systems RbBr–RbCl and RbBr–KBr at 25°C. according to Durham and Hawkins.

For the solid solution RbBr–RbCl, Durham and co-workers[44] give a lattice constant range of 6·5946 to 6·8900 for the composition range RbBr 3·78, RbCl 93·1, K(Br,Cl) 3·09mole% to RbBr 95·3, RbCl 0, K(Br,Cl) 3·18mole% at

TABLE I.- DATA FOR THE SYSTEMS RbBr–RbCl AND RbBr–KBr AT 25°C.

Mole fraction RbBr (N.)	Lattice Const.	Heat of mixing (ΔH g.-cal./mole)	Total energy of displacement per ion pair (g.-cal./mole)	Ratio mean ionic activity coeff. (mole fraction units)	Mole fraction RbBr (liquid) Exptl.
RbBr–RbCl					
·1	3·3108	181	−96	·284	·18
·3	3·3416	402	−208	·118	·3
·5	3·3722	451	−229	−·022	·38
·7	3·4018	355	−178	−·014	·51
·9	3·4304	139	−70	−·239	·74
RbBr–KBr					
·1	3·3146	150	−114	·128	·22
·3	3·3442	340	−256	·055	·42
·5	3·3735	377	−268	−·010	·53
·7	3·4019	295	−213	−·067	·63
·9	3·4298	117	−87	−·111	·82

temperatures varying between 28·3°C. and 26·1°C. and for the solid solution RbBr–KBr, a lattice constant range of 6·6284 to 6·8936 for a composition range RbBr 10 to 98·0; KBr 1·79, CsBr 0·21 mole%.

In the system RbBr–AgBr, the variation of e.m.f. with mole fraction of silver bromide and temperature for the cell Ag(s), AgBr(l), RbBr(l) Br_2(g) is as shown in Table II.

TABLE II.- ELECTROMOTIVE FORCE IN THE SYSTEM RbBr–AgBr.

Mole fraction AgBr	Temperature	e.m.f.
1·0	456—565	·7989—·7680
0·747	463—618	·8215—·7811
0·596	469—617	·8478—·8112
0·467	489—618	·8723—·8429
0·352	519—622	·9001—·8788

The densities of the solutions are calculated from the formula $d_t = 4{\cdot}470 - 0{\cdot}00123t$ and for a 0·5 mol. fraction of rubidium bromide in silver bromide, vary from 3·838 at 514°C. to 3·702 at 624°C. The author has also calculated entropy of formation, entropy change upon dilution or partial molal entropy, free energy of formation, free energy of dilution or partial molal free energy, heat of formation and heat of dilution, when silver bromide is diluted with rubidium bromide.[45]

In determining the refractive index of molten AgBr–RbBr solutions the molar refractivities of these solutions were found to be an additive function of the mole fraction.[46] Table III gives values found to determine the molar refractivity at infinite wave-length for various AgBr–RbBr solutions at 650°C. No strong new absorption bands were found as in aqueous solutions of AgBr–RbBr and so it is concluded that no "complex ions" exist in the melts. The absorption coefficient at 5850 A. is 1 cm.$^{-1}$ in a silver bromide melt containing 13% of rubidium bromide. Density calculations were made using the formula: $d_t = 3{\cdot}458 - 11 \times 10^{-4}t$.

Investigation of the phase diagrams of silver halides combined with the corresponding alkali halides has shown[47] that with the chlorides, lithium and sodium form solid solutions, potassium and rubidium form eutectics and

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TABLE III.- MOLAR REFRACTIVITY IN THE SYSTEM RbBr–AgBr.

Mole fraction AgBr	$\frac{n_\infty - 1}{n_\infty + 2}$	V c.c. Molar vol. of melt	R_∞ Molar refractivity at infinite λ
0	·2675	60·3	16·13
0·173	·2910	55·94	16·28
0·301	·3114	52·46	16·34
0·313	·3114	52·23	16·26
0·485	·3469	47·33	16·8 (extrapolated)

n_∞ = refractive index at infinite wave-length, $(n_\infty - 1)/(n_\infty + 2)$ being a linear function of temperature.

cæsium forms a peritectic; with the bromides lithium and sodium form solid solutions, potassium forms a eutectic and rubidium and cæsium peritectics, and with the iodides only lithium forms a solid solution, sodium a eutectic and potassium, rubidium and cæsium peritectics. This regularity is corroborated by experimental data in other systems such as $RbBr-PbBr_2$ and the change from one type of diagram to another is explained by the formation of complexes.

The free energy of formation of the binary solution RbCl–RbBr has been calculated from Wasastjerna's theory. The author lists entropies of formation, 4th. approximations of heats of formation and free energy values for increments of 0·1 mol. fraction of RbCl in RbBr and estimates the critical solution temperature to be 173·2°K. Fig. 1 shows the free energy-composition curves of the system at the four temperatures investigated.[48] In the systems RbCl–RbBr, KBr–RbBr in which the difference between the interionic equilibrium distances of the components, ΔR, is equal to or less than that in the case of NaCl–NaBr, the theoretical heat of formation data corresponding to the equilibrium at 50°C. are closely proportional to the expression $(\Delta R)^2/R_0^3$, where R_0 is the interionic distance of the solid solution.[49]

The free energy, F, of hydration of ions has been calculated by the semi-empirical formula: $F = Ne^2m^2(1 - 1/D)/(\gamma + \beta r^{1/2})$ where N = Avogadro's no., e = charge of the electron, m = charge of the ion, γ = radius of the ion, D = dielectric constant, $\beta r^{1/2}$ = distance between the ion and the nearest pole of the H_2O dipole. Empirically, from the known heats of solution and the lattice energies of sodium chloride and rubidium bromide, β = 0·83 and 0·23 for univalent cations and anions respectively. By calculating F, and using Latimer's values for the entropy of hydration, heats of hydration are determinable.[50] The total heat of hydration $H^\pm$ of rubidium bromide has also been selected on the basis of measurements of heats of solution at infinite or very high dilution, and values of lattice energy U, although the latter term involves an uncertainty of thermodynamic definition. The value given for the total heat of hydration of rubidium bromide is 145 kg.-cal./mole at 25°C. As a principle for the separation of $H^\pm$ into heats of solvation H^+ and H^- of the individual ions, Mishchenko rejects assumptions made by Bernal, Fowler and others of approximately equal H for ions of equal ionic radii, mainly on account of the dissymmetry of the location of the dipole moment of the H_2O molecule which is estimated to be about 0·25 A. Heats of solvation for Rb^+ and Br^- are given as 74 and 72 kg.-cal./g.-ion respectively. Co-ordination numbers, n, (number of water molecules surrounding the ion in the nearest solvate envelope) are for Rb^+, 8 and for Br^-, 8 and are evaluated from the known radii of the ions and the radius, r_w, of the water molecule. Satisfactory values have been obtained with r_w = 1·93 A. corresponding to liquid H_2O but not with r_w = 1·38 A., the radius of the water molecules in ice. The values are at considerable variance with those of Bernal, Fowler *et al.* who

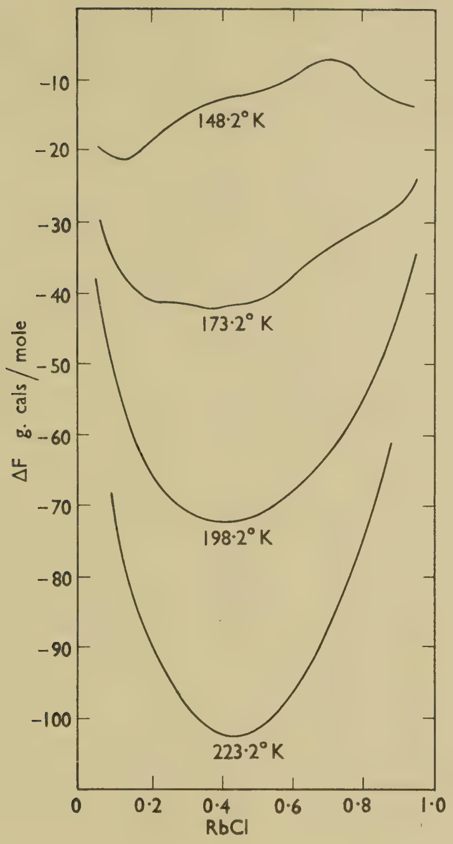

FIG.- 1. FREE ENERGY-COMPOSITION CURVES FOR THE BINARY SOLUTION RbCl–RbBr.

attribute $n = 4$ to all univalent ions on the assumption of a "frozen" hydrate envelope. The ratio of the heat of solvation, H, and the co-ordination number, n, gives the heats of interaction H_1 between the ion and one molecule of water in the solvate envelope as 9·2 kg.-cal./g.-ion for Rb^+ and 9·0 kg.-cal./g.-ion for Br^-. These values can be represented as functions of the ionic radii in the form: $\log H_1^- = (1{\cdot}38/r^-) + 0{\cdot}25$; $\log H_1^+ = (0{\cdot}70/r^+) + 0{\cdot}47$ and $(1/H_1^-) = 0{\cdot}1r^- - 0{\cdot}085$; $(1/H_1^+) = 0{\cdot}1r^+ - 0{\cdot}035$. Simple consideration of electrostatic interaction gives, per mol. H_2O, an energy of $127{\cdot}06 \times 10^{-16}/(r_i + r_w \pm \beta)^2$ kg.-cal./g.-ion. (β = dissymmetry of the location of the dipole moment in the water molecule, estimated as 0·25 A.). Values calculated with this formula are in very fair agreement with experimental values of H_1 for Rb^+ and Br^-, with $\beta = 0{\cdot}25$ A. and $r_w = 1{\cdot}93$ A. The effective radii of water molecules in the hydrate envelope of Rb^+ and Br^- have been calculated to be 1·97 A. and 2·05 A. respectively, which, being greater than 1·93, indicate an expansion of the hydrate envelope.[51]

From standard electrode potentials of bromine and rubidium and from relevant standard free energy data, Kanevskiǐ has calculated the standard free energy of hydration of the pair of ions Rb^+ and Br^- to be 139·7 kg.-cal./mol.[52]

Investigations of the limit of full solvation of rubidium bromide in concentrations of 4·63 to 2·14 moles/1000 g. of water have shown that the distance between centres of ions in solutions at the limit of full solvation, calculated from the density of the solutions, is in good agreement with that found from models of the solutions at the limit of full solvation. The exothermic effect when ions are brought from zero to full solvation is calculated as +39 kg.-cal./mole for rubidium bromide.[53]

The integral heats of solution, $L_m^{D_2O}$, $L_m^{H_2O}$ of rubidium bromide in D_2O and H_2O are −6·048 and −5·313 kg.-cal./mol. of salt respectively. The difference in heats of solution ($L_m^{D_2O} - L_m^{H_2O} = \Delta L$), called the "isotopic effect", is −0·735 kg.-cal./mole of salt. The differences in "isotopic effect" of two similarly charged ions, e.g. Cl^-, and Br^-, calculated from the corresponding values of ΔL, are independent of the common oppositely charged ion.[54]

The supersaturation limits for rubidium bromide in aqueous solution have been calculated from the equation: $T_s - T = 13\sigma V_m/\lambda$ where T_s = absolute saturation temperature, T = absolute temperature of 1st spontaneous crystallisation, σ = specific surface energy, V_m = molar volume, λ = heat of solution.

Experimental values given are: $\lambda = 5960$, $\sigma = 138$, $\sigma V_m = 6979$ giving $T_s - T = 15{\cdot}2$°C., but no great accuracy is claimed for these results. The radius of the stable crystal nucleus at the first temperature of spontaneous crystallisation is shown to be of the order of 10^{-6} cm. and varies hyperbolically with the degree of supersaturation.[55] Attempts have been made to correlate the solubility of rubidium bromide with the dielectric constant of the solvent in the case of water, acetone and a number of alcohols, but because of the many factors involved no general rule has been established.[56] The solubility of rubidium bromide in absolute acetone decreases with increasing temperature.[57] Table IV[58] gives the solubilities of rubidium bromide in methyl alcohol, acetonitrile and formic acid.

TABLE IV.- SOLUBILITY OF RUBIDIUM BROMIDE IN ORGANIC SOLVENTS.

	Methyl Alcohol			Acetonitrile			Formic Acid		
	d	*s*	*c*	*d*	*s*	*c*	*d*	*s*	*c*
18°C.	·806	10·1	0·37	·798	1·8	$6{\cdot}8 \times 10^{-2}$	1·58	46	2·3
25°C.	·859	10·1	0·37	·793	1·6	$6{\cdot}2 \times 10^{-2}$	1·58	47	2·3

d = density; *s* = solubility in g./100 g. solvent; *c* = concentration in moles/litre.

The solubility of rubidium bromide in liquid sulphur dioxide is 20% at 25°C. Because of the inverse order of the solubilities of the halides of rubidium and caesium and of the other alkali halides in sulphur dioxide and liquid ammonia, successive recrystallisations from these solvents can be used to separate rubidium and caesium from the other alkali metals.[59] The molar heat effect of RbBr in NH_3 is[60] 440 g.-cal./mole.

The solubility of ethyl acetate in g. per 100 g. H_2O in 0·397 M. rubidium bromide solution is 7·41% at 30°C. and 7·13% at 35°C. and in 0·194 M. rubidium bromide solution is 7·20% at 30°C. and 6·86% at 35°C. The experimental activity coefficients in 0·097 M. and 0·194 M. rubidium bromide solutions are 1·039 and 1·070 respectively.[61]

Table V gives the variations of osmotic and activity coefficients with concentrations for aqueous solutions of rubidium bromide. Figures vary only slightly from earlier values published by Robinson.[62]

The equivalent dispersion of an aqueous solution of rubidium bromide in the ultra-violet decreases with increasing salt concentration.[63] *X*-Ray diffraction patterns of a saturated solution of rubidium bromide show a broad ring with its position independent of concentration. This ring is ascribed mainly to interference between the scattering from a heavy ion and that from the surrounding water molecules.[64] The scattering of Cu *K* radiation in

TABLE V.- OSMOTIC AND ACTIVITY COEFFICIENTS FOR AQUEOUS SOLUTIONS OF RUBIDIUM BROMIDE.

m (moles/1000 g. H_2O)	Osmotic coefficient ϕ	Activity coefficient γ
·1	·922	·763
·2	·905	·706
·3	·897	·673
·4	·892	·650
·5	·888	·632
·6	·886	·617
·7	·884	·605
·8	·882	·595
·9	·881	·586
1·0	·881	·578
1·2	·880	·565
1·4	·881	·556
1·6	·882	·547
1·8	·884	·541
2·0	·887	·536
2·5	·893	·526
3·0	·899	·520
3·5	·907	·516
4·0	·916	·514
4·5	·924	·514
5·0	·934	·515

solutions of rubidium bromide at concentrations up to 5·16 mol./litre is compatible with the assumption of a random distribution of ions in the solution. The data indicate that water has a distorted lattice structure in which the ions are located. At high concentrations, the scattering of water is repressed and the whole structure becomes similar to that of solid rubidium bromide containing water.[65]

The dissociation constant of rubidium bromide in aqueous solution calculated from the conductivity according to the Jablczynski and Wisniewski equation for mass action agrees well with the constant calculated from ebullioscopic data. This equation is preferred to that of Kohlrausch, which is claimed to give inconstant values, and to that of Debye and Hückel since it gives very satisfactory agreement up to concentrations of 3 N. while the equation of Debye and Hückel does not apply above 0·01 N.[66]

The maximum specific conductivity of the system RbBr–$AlBr_3$ in ethyl bromide at 18°C. is 2·37 (reciprocal ohms × 10^3) corresponding to a concentration of rubidium bromide = 0·861% by weight. On the basis of this and other data it is concluded that the conductivity of an ethyl bromide solution of aluminium bromide increases with increasing concentration of a bromide of a metal in the first group of the Periodic Table, and decreases with dilution, rubidium bromide being less effective than the bromides of silver, lithium, copper or potassium. Electrolysis of the system $AlBr_3$–RbBr–EtBr deposits aluminium at the cathode. The decomposition voltage of rubidium bromide is 1·66 V.[67] The specific conductivity of the system $AlBr_3$–RbBr in benzene and toluene also increases with addition of bromides of metals in Group I of the Periodic Table. Electrolysis of the systems produces aluminium at the cathode, but if the electrolysis is carried out in nitrobenzene the alkali metal is deposited. It is postulated that the electric conductance depends on the solute and the solvent, the two substances forming a conducting pair. Polymerization and complex formation are said to influence the solubility of the electrolytes.[68]

When rubidium bromide is electrolysed in acetic anhydride, deposition at the anode does not apparently occur in accordance with Faraday's Law, for while the theoretical quantity of hydrogen is obtained, the yields of rubidium and bromine are low. The variation is ascribed to a secondary reaction of the primary product with the solvent.[69] Electrolysis of rubidium bromide in anhydrous acetic acid using a silver anode gives a quantitative yield of silver bromide.[70]

The addition of rubidium bromide at 0°C. strongly catalyzes the sulphur exchange between thionyl bromide and sulphur dioxide. The catalysis is homogeneous, with exchange rates apparently of first order as to catalyst concentration and zero order as to thionyl bromide concentration. The value of k for rubidium bromide in the expression: rate = k × catalyst concentration is comparable with that for cæsium chloride, rubidium chloride and tetramethylammonium bromide, approximately 6×10^{-3}/min. at 0°C. The reaction is interpreted as involving basic catalysis by halide ions.[71]

Study of the conditions favourable for the formation of solid solutions has shown that precipitates may be contaminated by substances of similar electronic arrangement which constitute a source of error in the precipitation operations of analytical chemistry. Investigation of silver bromide precipitated in presence of rubidium bromide has shown that in the short time that normally elapses between the formation of the precipitate and its removal by filtration there is not usually any appreciable quantity of solid solution formed from which the water soluble constituent cannot be removed by washing; if, however, the precipitate is allowed to remain indefinitely in the mother liquor serious errors may arise owing to the formation of a solid solution.[72] Measurement of the adsorption of rubidium bromide at 25°C. by lead sulphide precipitated from a 0·01 M. solution saturated with lead sulphide and lead sulphate, indicates that the amount adsorbed does not depend on the ability of the adsorbed compound to fit the space lattice of the adsorbent, or on the ability of lead sulphide to orient the crystallisation of the salt. The amount adsorbed increases as the mole fraction solubility of the salt in water decreases. The order of increasing adsorption of the alkali halides is $LiBr < NaBr < NH_4Br < RbBr < CsBr < KBr$.[73]

Examination of the absorption and accumulation of rubidium bromide by living plant cells (potato discs) has shown that in the first phase, rubidium is rapidly taken up, unaccompanied by bromine. The second phase occupies a long period during which both rubidium and bromide are absorbed in equivalent amounts.[74]

In the ternary system magnesium bromide–rubidium bromide–water at 25°C., no compounds or solid solutions are formed, and the isotherm consists of a very extended rubidium bromide branch and a much shorter magnesium bromide hexahydrate branch. Rubidium bromide is almost completely salted out by the magnesium bromide saturated solution which contains only traces of rubidium bromide in equilibrium with rubidium bromide and magnesium bromide hexahydrate. Addition of magnesium bromide to solutions of rubidium bromide decreases sharply the solubility of the latter. The solubility of rubidium bromide in water is given[75] as 53·35% at 25°C.

In the systems rubidium bromide–rubidium chloride–water and rubidium bromide–potassium bromide–water, both ternary systems show formation of type II solid solutions, according to Roozeboom's classification.[76] Fig. 2 shows the distribution of rubidium bromide between aqueous and solid solutions for the two systems.

The solubility in water of rubidium bromide (52·9% at 25°C.) is reported as appreciably lower than that given by Seidell (53·7%). Janecke[77] has studied

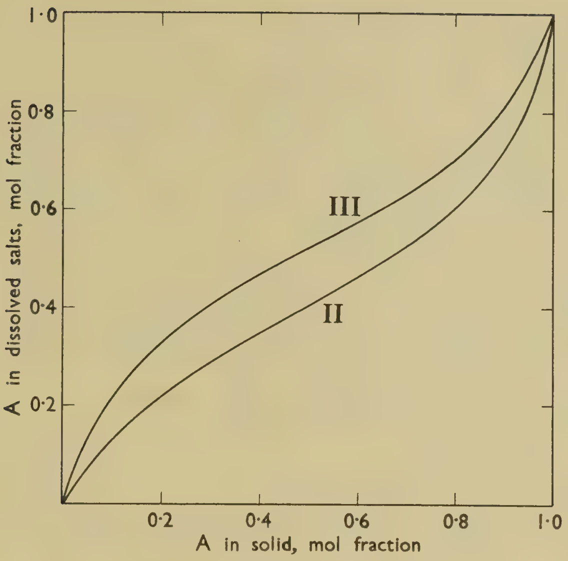

FIG. 2.- DISTRIBUTION BETWEEN AQUEOUS AND SOLID SOLUTION AT 25°C.
II RbBr (A) – RbCl; III RbBr (A) – KBr.

the changes of the composition of the solid phases and the mother liquors, and the complete or partial formation of solid solutions of salts in saturated solutions in the system (K, Rb) (Cl, Br)–H_2O at 25°C.

Chemical Properties

A double salt, $RbBr,MgSO_4$, of the type $KCl,MgSO_4$, has been obtained. The electrical conductivity of the fused kainite system has a sharp minimum at the molar ratio 1:1, thus indicating a decrease in the number of ions. *i.e.* persistence of the complex ions characteristic of kainite even in the fused state. The electrolytic dissociation is probably $RbBr,MgSO_4 \rightleftharpoons Rb^+ + [BrMgSO_4]^-$. The formation of the salt is thus contingent on the relative attractions of Rb^+ and Mg^{++} for Br^- and is determined by the generalized moment $\mu = Z/r$ where Z = charge and r = radius of the ion.[78]

RUBIDIUM POLYBROMIDES AND BROMOHALIDES

Pressure measurements at various temperatures indicate[79] a reaction between rubidium bromide and bromine and the existence of rubidium tribromide which decomposes in the range 35°C. to 78°C.

A solution of rubidium bromide in iodine bromide shows high conductivity and studies by conductimetric titration indicate,[80] in the presence of stannic bromide, the reaction: $2RbIBr_2 + SnBr_2 \rightleftharpoons Rb_2SnBr_2 + 2IBr$.

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SECTION LXXI

RUBIDIUM IODIDE

By N. R. W. BENWELL

Physical Properties

The following physical properties of the rubidium iodide crystal have been calculated from a statistical atomic model made without any empirical or semi-empirical parameters: lattice constant, $3{\cdot}69 \times 10^{-8}$ cm.; compressibility, $8{\cdot}45 \times 10^{-12}$ sq.cm./dyne, infra-red wave-length, 124×10^{-4} cm.; tensile strength, $1{\cdot}52 \times 10^{10}$ dynes/sq.cm.[1]

The cubic compressibility of rubidium iodide is $9{\cdot}3 \times 10^{-6}$ per megabar as derived from the semi-empirical formula $\beta = kV_m/U$ where β = compressibility; k = empirical constant; V_m = molecular volume; U = molecular heat of formation of the salt. This equation is considerably more accurate than that of Born derived from consideration of the Bohr theory of atomic structure.[2] The compressibilities of rubidium iodide under 50,000 kg./sq.cm. at room temperature and at the temperature of solid carbon dioxide are 0·3009 and 0·2921 respectively. A transition occurs[3] at 4050–5000 kg./sq.cm. The following details of the compressibility of rubidium iodide have been determined by Bridgman's method: (1) compressibility at 30°C.:- $9{\cdot}58 \times 10^{-12}$; (2) compressibility at absolute zero by extrapolation:- $7{\cdot}6 \times 10^{-12}$; (3) change of compressibility with pressure independent of temp. between 30°C. and 75°C. $43{\cdot}0 \times 10^{-12}$ and (4) average change of compressibility with temperature between 30°C. and 75°C. $6{\cdot}8 \times 10^{-4}$. As would be expected, the change of compressibility with temperature is related to the thermal expansion in such a way that an increase in temperature and decrease in pressure have the same effect on both volume and compressibility.[4] Rubidium iodide at 4500 kg./sq.cm. and room temperature is body centred cubic, with a lattice constant of 4·33 A. The volume change from the face-centred lattice, which is stable below 4000 atm., is[5] 0·037 c.c./g. A further expression for compressibility is given by Szigeti:[6]

$$\frac{1}{\kappa} = \frac{R^2}{3v} \cdot \frac{\epsilon + 2}{n^2 + 2} m\omega_t^2$$

where ω_t = absorption frequency; R = nearest neighbour distance; κ = compressibility; v = volume occupied by an ion pair; ϵ = dielectric constant; n = optical refractive index; m = reduced mass of the ion pair. The following values have been obtained for the equation applied to rubidium iodide:

Type	R	$R^2/_3$	ϵ	n^2	$m\omega_t^2$	κcalc.	κobs.	κc/κo
	(10^{-8} cm.)	(10^6 cm.)			(10^4 dynes/cm.)	(10^{-6} cm.^{2}/kg.)		
NaCl	3·66	4·56	5	2·63	2·3	6·17	9·39	0·66

The root mean square amplitude of atomic vibration for rubidium iodide crystal at 293°K. is given as 0·32 (Lonsdale).[7] The frequencies and anharmonicities of the lattice oscillations of rubidium iodide, *i.e.*, the oscillations of the interpenetrating lattice of the rubidium and iodine ions with respect to one another have been calculated on the basis of the Born model. The calculated value of the frequency of lattice oscillation, $2{\cdot}3 \times 10^{-12}$ (Krishnan and Roy) is in exact agreement with the observed value of $2{\cdot}3 \times 10^{-12}$ (Barnes). The anharmonicity of the lattice oscillations, unlike its frequency, varies with the direction of the oscillation from a large positive value along [111] to a small negative value along [100].[8]

A new region of anomalous electrical response is observed at low frequencies in ionic crystals of a number of univalent halides including rubidium iodide. The effect is attributed[9] to a jumping of the positive ions to vacant lattice sites under the influence of the applied field. The jumping is observed as a relaxation process, producing a change in the dielectric constant which is small and frequently within the limits of error of measurement, and an associated peak in the dielectric-loss tangent which is readily measurable. From the magnitude of the peak ($\tan \delta_{\text{max.}}$) and its position on the frequency or temperature scales is calculated the number of lattice defects in the crystal and the activation energy of diffusion, U, of the positive ion. A knowledge of U leads to separation of the activation energy for conduction, $(W/2) + U$, into its components, and thus W, the activation energy for hole formation is determined. For rubidium iodide at −135°C., and a frequency of 10^4 cycles/sec., $U = 0{\cdot}21$ e.V., $W/2 + U = 1{\cdot}84$ e.V., $W = 3{\cdot}26$ e.V. The time constant for the natural frequency of lattice vibrations $= 0{\cdot}43$ sec. $\times 10^{12}$.

Microscopical observation of the crystal growth of rubidium iodide (parameter 7·32 A.) on grease-free potassium chloride, rock salt and Joplin galena shows that the overgrowths are not oriented on any of these substrata. Ease of orientation appears to depend on the dissymmetry as measured by the ratio of anion to cation radius.[10]

X-Ray measurements made by the photographic powder crystal method have given a value for the length of side of a unit cube of rubidium iodide of 7·325 A. The effect of small amounts of isomorphous impurities (less than 1%) on the length of side of the unit body-centred cube is negligible.[11]

Following investigations of deposited overgrowths of alkali metal halides including rubidium iodide, Smollett and Blackman[12] have deduced the elastic constants of the two dimensional ionic lattice strained to fit onto the cube face of a substrate of the rock-salt type; these lead to conclusions that disagree with a suggestion of Frank and van der Merwe as to the general mechanism of oriented overgrowth. Instability is found in the initially deposited layer if this is strained to fit the substrate. The orientation observed in experiment cannot arise from an initially uniformly strained layer. It seems reasonable therefore to suppose that orientation is associated with an initially "distorted" lattice, where by "distortion" is meant any type of displacement of a lattice particle from its original position leaving the mean lattice spacing more or less constant. Rubidium iodide crystallised from aqueous solution on glass or on barium stearate layers on glass forms cubic crystals, whereas on mica the crystal outline is mostly an equilateral triangle with sides parallel to the traces of the (010), (110) and ($1\bar{1}0$) planes of mica, the (111) plane of rubidium iodide being parallel to the (001) plane of mica. If the crystallisation is effected on barium stearate layers deposited on mica, the proportion of unorientated cubic crystals increases with the thickness of the barium stearate layer. Layers nine molecules thick appear sufficient to eliminate the effect of the mica completely.[13] Schulz has shown that when rubidium iodide is grown onto muscovite cleavage surfaces, electron diffraction patterns taken in two positions differing by 30° indicate that salts like rubidium iodide with $a_0 > 5{\cdot}32$ A. show a double positioned type of angular orientation when grown from the vapour phase, but only a single positioned orientation when grown from solution.[14] When rubidium iodide (NaCl-type structure) is grown from the vapour phase onto cleavage surfaces of lithium fluoride, sodium chloride, potassium chloride and potassium bromide, electron diffraction patterns have shown that the

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crystals of the initial deposit are oriented with their crystallographic axes parallel to those of the substrate in all cases.[15] When grown from vapour or from solution on the cleavage faces of calcium carbonate or sodium nitrate, rubidium iodide shows well defined patterns in deposits 10 A. thick, but with thicknesses greater than 150 A., random orientation occurs. Factors important for controlling the orientation are: (1) low index planes lie parallel to the substrate surface (2) the contact planes usually contain ions of both signs, and (3) dimensions along rows of like ions must match. Growths from vapour and from solution do not always show the same orientation or even the same crystal structure.[16] Investigation of the effect of the rate of evaporation of non-aqueous solutions of rubidium iodide on the crystal faces developed has shown that only cubes are produced by slow evaporation from methyl alcohol, ethyl alcohol, acetone, acetophenone and dioxan, whereas an increased rate of evaporation produced octahedra except in the case of dioxan where the (111) face was not observed. The critical rate of evaporation necessary to produce octahedra (111) increases in the order MeOH, EtOH, Me_2CO, MeCOPh. The rate of formation of octahedra increases with the dielectric constant of the solvent.[17]

The dielectric constant of rubidium iodide is 5·58, as determined by Starke's method.[18] Recent calculations of the dielectric constant of rubidium iodide by various methods differing in the evaluation of the ionic polarizability have given values in satisfactory agreement with experimental data. The evaluation is based on the calculation of an elastic force coefficient, *k*, between opposed ions as the second derivative of the repulsion energy, from formulae of the type: $k = 1{\cdot}16(n-1)q^2/r_n^3$ where n = exponent of repulsion energy law; q = charge of the ion; r_0 = nearest distance in the lattice.[19]

In investigating the mechanical stresses in dielectrics in electrical breakdown, if the breakdown potential of rubidium iodide is plotted as a function of the pressure developed in the dielectric crystal through the application of the electric field just before the breakdown, it has been found[20] that with pressure increasing in a definite order the breakdown potential increases rapidly at first. This indicates that the weakening of the mechanical strength due to the high pressure results in a lowering of breakdown potential. On the other hand, the stress increases with increasing lattice energy. A practical inference is that increased mechanical strength should result in an increased dielectric strength. In further considering the electric breakdown of solid dielectrics, the same author[21] had assumed that breakdown takes place when the energy accumulated by the electrons and transferred to the rubidium iodide lattice is sufficient to break the bond between the lattice points, but experimental data did not bear this out, indicating more nearly a linear relation between field strength and lattice energy and a dissociation of the lattice into ions and not into neutral atoms. The decrease of the time interval between electron collisions with increasing electric field strength holds only at sufficiently high field strengths; possibly when the kinetic energy of the electrons becomes comparable with the vibration energy of the lattice points. The dielectric constant of rubidium iodide expressed in terms of the close packing of the lattice and of the valence bond is in good agreement with that calculated from lattice energy data.[22] When the dielectric strengths of rubidium halides are plotted with respect to heats of formation in the solid and gaseous states, straight lines of positive slope are obtained.[23] The value of the dielectric strength of rubidium iodide is given as 0·5 m.V./cm.

In investigating magnetic resonance shifts in the alkali metal halides, Ramsey has shown that chemical shifts result from precessional motions induced by the applied magnetic field in the electrons surrounding the nucleus. This precessional motion produces a small local field at the nucleus in opposition to the applied field and this local field will vary from molecule to molecule as a result of the variations in electronic structure. 100% ionic compounds have no chemical shifts and so the shielding change observed for rubidium iodide indicates that there is some covalent character in the crystalline bond. The chemical shift of the ^{87}Rb magnetic resonance $\Delta\sigma = (H_s - H_r)/H_r \times 10^4$ where H_s and H_r are the magnetic fields necessary for resonance at a fixed frequency for the sample and reference respectively is −1·49 for rubidium iodide, the reference being a saturated aqueous solution of rubidium chloride. The magnetic shielding of the alkali metals decreases from the fluoride to the iodide while the ion in solution has the largest shielding of all. The smaller shifts of rubidium support the observation that the chemical shifts decrease with decreasing nuclear charge.[24]

In investigating the thermal conductivity of a crystal lattice, consideration of the anharmonic properties of a linear chain has led to the suggestion that the dimensionless quantity $\alpha\gamma T$ is in general a measure of the anharmonicity of a lattice (α is the thermal expansion coefficient and γ is the Grüneisen parameter). It has therefore been proposed that the mean free path for lattice vibration in an insulator should, in the classical temperature region, be approximately $A_0/\alpha\gamma T$ where A_0 is the lattice spacing, and reasonably good agreement with experiment has been found for a number of alkali metal halides including rubidium iodide.[25]

Results of optical investigations of the state of gas molecules in the adsorption layer of solid rubidium iodide have shown that the spectral regions of photochemical activities are displaced slightly in the direction of smaller frequencies as compared with the positions of the corresponding regions for the gas molecules.[26]

When the heats of formation and of evolution are calculated on the basis of Wasastjerna's statistical theory for a binary alkali metal halide solid solution such as KI–RbI in which the difference between the interionic equilibrium distances of the components ΔR is equal to or smaller than that in the case of NaCl–NaBr, the theoretical heat of formation data corresponding to the equilibrium at 50°C. are in the case of KI–RbI, closely proportional to the expression $(\Delta R)^2/R_0^3$ where R_0 is the interionic distance of the solid solution.[27] Measurement of the thermal dissociation of rubidium iodide vapour with apparatus permitting separate measurements of the positive ion, negative ion and electron concentrations in the temperature range 1300–1500°C., and deduction of the equilibrium constants of dissociation have given a calculated value of 99·1 kg.-cal. for the heat of ionic dissociation of rubidium iodide. The lattice energy has been calculated to be 145·5 kg.-cal.[28] The heat of vaporisation of rubidium iodide determined[29] from the expression $\lambda = -1{\cdot}985 \times 2{\cdot}303 \times [d \log p/d(1/T)]$ is[31] 36,870 g.-cal. The same author has given a boiling point of 1304°C. by calculation or extrapolation of vapour pressure data, and a critical temperature = 2444°K. Greater accuracy is claimed for these results than for those calculated by the Ramsay–Young rule. For gaseous rubidium iodide, the interatomic distance = 3·23 A., fundamental frequency = 179 cm.$^{-1}$ and entropy ($S_{298\cdot1}$) = 61·8 g.-cal./degree, the uncertainty being ± 0·3 e.V.[30] The vapour pressure curves of the alkali iodides at temperatures between the boiling point and 200–300°C. below the boiling point of the salt lie closer together than those of the alkali salts of halogens of lower atomic weight.[31]

Measurements of the specific heats, C_p and C_v of rubidium iodide by vacuum calorimetry show a rise of specific heat at constant pressure from 0·64 at 11·6°K. to 6·28 at 276·9°K. and of the specific heat at constant volume from 1·27 at 16·2°K. to 5·97 at 276·9°K., and in this temperature range the characteristic Debye temperature, θ, varies between 100 and 118, thus deviating from the prediction of the Debye theory that θ is constant.[32]

Using the latest data on dispersion and adsorption, a dispersion formula of the Drude form has been developed[33] for rubidium iodide: $n^2 = 1{\cdot}6017 + [0{\cdot}01749\lambda^2/(\lambda^2 - 0{\cdot}015625)] + [0{\cdot}83466\lambda^2/(\lambda^2 - 0{\cdot}033948)] + [0{\cdot}13917\lambda^2/(\lambda^2 - 0{\cdot}049729)]$.

When silver halides are combined with the corresponding halide of the alkali metals, the phase diagrams show certain regularities. With the chlorides, lithium and sodium form solid solutions, potassium and rubidium form eutectics and cæsium forms a peritectic; with the bromides, lithium and sodium form solid solutions, potassium forms a eutectic and rubidium and cæsium peritectics, and with the iodides only lithium forms a solid solution, sodium a eutectic and potassium, rubidium and caesium, peritectics. The change from one type of diagram to the other is explained by the formation of complexes.[34]

The total heat of hydration $H^{\pm}$ of rubidium iodide has been selected on the basis of measurements of heats of solution at infinite or very high dilution and values of lattice energy, U, although the latter term involves an uncertainty in thermodynamic definition. The value given for rubidium iodide is 137 kg.-cal./mole at 25°C. As a principle for the separation of $H^{\pm}$ into heats of solvation H^+ and H^- of the individual ions, Mishchenko rejects assumptions made by Bernal, Fowler and others of approximately equal H for ions of equal ionic radii, mainly on account of the dissymmetry of the location of the dipole moment of the H_2O molecule which is estimated to be about 0·25 A. Heats of solvation for Rb^+ and I^- are given as 74 and 63 kg.-cal./g.-ion, respectively. Co-ordination numbers, n, (number of water molecules surrounding the ion in the nearest solvate envelope) are for Rb^+ 8 and for I^- 8 and are evaluated from the known radii of the ions and the radius r_w of the water molecule. Reasonable values have been obtained with $r_w = 1{\cdot}93$ A., corresponding to liquid H_2O, but not with $r_w = 1{\cdot}38$, the radius of water molecules in ice. The values are at considerable variance with those of Bernal, Fowler and others who attribute $n = 4$ to all univalent ions on the assumption of a "frozen" hydrate envelope. The ratio of the heat of solvation H and the co-ordination number n gives the heats of interaction H_1 between the ion and one molecule of water in the solvate envelope as 9·2 kg.-cal./g.-ion for Rb^+ and 7·9 kg.-cal./g.-ion for I^-. These values can be represented as functions of the ionic radii in the form: $\log H_1^- = (1{\cdot}38/r^-) + 0{\cdot}25$; $\log H_1^+ = (0{\cdot}70/r^+) + 0{\cdot}47$ and $(1/H_1^-) = 0{\cdot}1r^- - 0{\cdot}085$; $(1/H_1^+) = 0{\cdot}1r^+ - 0{\cdot}035$. Simple consideration of electrostatic interaction gives, per mol. H_2O, an energy of $127{\cdot}06 \times 10^{-16}/(r_i + r_w \pm \beta)^2$ kg.-cal./g.-ion. (β = dissymmetry of the location of the dipole moment in the water molecule, estimated as 0·25 A.). Values calculated with this formula are in very fair agreement with the experimental values of H_1 for Rb^+ and I^- with $\beta = 0{\cdot}25$ and $r_w = 1{\cdot}93$ A. The effective radii of water molecules in the hydrate envelope of Rb^+ and I^- have been calculated to be 1·97 A. and 2·09 A., respectively, which, being greater than 1·93, indicate an expansion of the hydrate envelope.[35]

From standard electrode potentials of iodine and rubidium and from relevant standard free energy data, Kanevskiĭ[36] has calculated a value of 132·7 kg.-cal./mole^{-1} for the standard free energy of hydration of the pair of ions Rb^+ and I^-.

Investigations of the limit of full solvation of rubidium iodide in concentrations of 4·63 to 2·14 moles/1000 g. of water have shown that the distance between centres of ions in solutions at the limit of full solvation, calculated from the density of the solutions, is in complete agreement with that calculated from models of the solutions at the limit of full solvation, the value being 8·15 A. The exothermic effect when ions are brought from zero to full solvation has been calculated to be + 39 kg.-cal./mole for rubidium iodide.[37]

The supersaturation limits for rubidium iodide in aqueous solution are calculated from the formula: $T_s - T = 13\sigma V_M/\lambda$ where T_s = absolute saturation temperature, T = absolute temperature of first spontaneous crystallisation, σ = specific surface energy, V_M = molar volume, λ = heat of solution.

Experimental values given are: $\lambda = 6500$; $\sigma = 126$; $\sigma V_M = 7862$, giving $T_s - T = 15{\cdot}6$, but no great accuracy is claimed for these results. The radius of the stable crystal nucleus at the first temperature of spontaneous crystallisation is shown to be of the order of 10^{-6} cm. and varies hyperbolically with the degree of supersaturation.[38]

When water is supercooled, the presence of rubidium iodide is claimed to have no effect upon the lowest temperature attained before spontaneous freezing takes place, *i.e.* upon the extent of supercooling.[39]

The solubility of rubidium iodide in certain organic liquids is shown in Table I.[40]

TABLE I.- SOLUBILITY OF RUBIDIUM IODIDE IN METHYL ALCOHOL, ACETONITRILE AND FORMIC ACID.

	Methyl Alcohol			Acetonitrile			Formic Acid		
Temp.	*d*	*s*	*c*	*d*	*s*	*c*	*d*	*s*	*c*
18°C.	0·806	10·1	0·37	0·798	1·8	$6{\cdot}8 \times 10^{-2}$	1·58	46	2·3
25°C.	0·859	10·1	0·37	0·793	1·6	$6{\cdot}2 \times 10^{-2}$	1·58	47	2·3

d = density; *s* = solubility in g./100 g. of solvent; *c* = concentration in mols./litre.

The solubility of ethyl acetate in aqueous solutions of rubidium iodide is given in Table II. The experimental activity coefficients of ethyl acetate in ·099 M. and ·189 M. rubidium iodide solution are 1·016 and 1·013 respectively.[41]

TABLE II.- SOLUBILITY OF ETHYL ACETATE IN AQUEOUS SOLUTIONS OF RUBIDIUM IODIDE.

Concn. RbI	20°C.	25°C.	30°C.
·099 M.	8·42	8·0	7·58 g. ethyl acetate/100 g. H_2O
·189 M.	8·41	8·01	7·60 g. ethyl acetate/100 g. H_2O

Attempts have been made[42] to correlate the solubility of rubidium iodide with the dielectric constant of the solvent in the case of water, acetone and a number of alcohols, but because of the many factors involved no general rule has been established. The solubility in absolute acetone is said to decrease with increasing temperature. Other workers[43] give the solubility in weight per cent. from −80°C. to +40°C. by the formula: $1{\cdot}15 - 2{\cdot}13 \times 10^{-2}t + 1{\cdot}54 \times 10^{-4}t^2$.

Table III[44] gives the variations of osmotic and activity coefficients with concentration for aqueous solutions of rubidium iodide. The figures differ only slightly from earlier values published by Robinson.

TABLE III.- VARIATION OF OSMOTIC AND ACTIVITY COEFFICIENTS WITH CONCENTRATION AT 25°C. IN AQUEOUS SOLUTIONS OF RUBIDIUM IODIDE.

m (moles/1000 g. H_2O)	Osmotic coefficient ϕ	Activity coefficient γ
·1	·921	·762
·2	·904	·705
·3	·896	·671
·4	·890	·647
·5	·886	·629
·6	·884	·614
·7	·881	·602

continued on following page

TABLE III.- CONTINUED.

m (moles/1000 g. H_2O)	Osmotic coefficient ρ	Activity coefficient γ
·8	·880	·591
·9	·879	·583
1·0	·878	·575
1·2	·878	·562
1·4	·878	·551
1·6	·880	·544
1·8	·882	·537
2·0	·886	·533
2·5	·893	·524
3·0	·901	·518
3·5	·911	·516
4·0	·921	·515
4·5	·931	·516
5·0	·940	·517

The data given in Table IV for the conductivity of rubidium iodide in ethyl alcohol at 25°C. show that the decrease in conductivity is proportional to the square root of the equivalent concentration, in agreement with the theory for strong electrolytes.[45]

TABLE IV.- ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF RUBIDIUM IODIDE IN ETHYL ALCOHOL.

κ	$c \times 10^4$	$100\sqrt{c}$	Λ_c	Difference
0·042	0·656	0·810	49·55	−·40
	1·316	1·148	49·17	−·01
	2·254	1·501	48·47	+·09
	3·102	1·762	47·92	+·13
	4·340	2·083	47·14	+·09
0·022	0·842	0·918	49·33	−·38
	1·592	1·261	48·88	−·04
	2·761	1·661	47·99	−·02
	3·763	1·940	47·38	0
	5·111	2·261	46·60	−·05

$c \times 10^4$ = concentration in g.-equiv./litre, density assumed the same as for the pure solvent. κ = specific conductivity in reciprocal megohms (with solvent correction). Λ_c = observed equivalent conductivity. Column 5 gives the difference between the observed equivalent conductivity and that calculated from the equation: $\Lambda_c = \Lambda_0 - x\sqrt{c}$, where $\Lambda_0 = 51{\cdot}8$ and $x = 228$.

Table V gives values of equivalent conductances and conductance ratios for rubidium iodide in furfural, the value of the limiting conductance being determined by extrapolation. The ratios are relatively high, indicating that furfural is a solvent possessing high dissociating power.[46]

The furfural solutions do not conform to the relation deduced by Walden, *viz.* $\kappa = \eta_0 D(v)^{0{\cdot}45} d_v = 51{\cdot}4$, where η_0 = viscosity of solvent, D, the dielectric constant, $(v)^{0{\cdot}45}$ the dilution and $d_v = \Lambda_0 - \Lambda$. With $\eta_0{}^{25°C.} = 0{\cdot}0149$ and $D_{25} = 38$, dilutions of 500, 1000 and 2000 give values of 12·68, 12·13 and 12·91 for K. The degree of solvation of the cation Rb^+ is 0·67, approximately of the same order of magnitude as in aqueous solution. The variation in the conductance of the rubidium iodide solution in furfural with concentration is accurately expressed by the Storch equation: $\Lambda_0 - \Lambda = \kappa \Lambda^n C^{n-1}$. The

TABLE V.- CONDUCTANCE OF SOLUTIONS OF RUBIDIUM IODIDE IN FURFURAL.

c	v	Λ	$a = \Lambda/\Lambda_0$
0·07	14·29	33·33	0·74
·06	16·67	34·10	·758
·05	20·00	34·95	·776
·02	50·0	39·00	·867
·01	100·0	41·10	·913
·005	200·0	42·40	·942
·002	500·0	43·50	·967
·001	1000·0	44·00	·978
·0005	2000·0	44·30	·985
0·0	∞	(45·00)	1·000

c = concentration, mols/litre; v = corresponding volume;
Λ = equivalent conductance; Λ_0 = limiting conductance.

exponent n varies with experimental data, being greater for furfural than for the corresponding aqueous solutions.

The e.m.f. of the cell Rb|0·01 N. RbI in CH_3CN|0·01 N. $AgNO_3$ in CH_3CN|Ag at 25°C. is 2·3275 volts. Temperature coefficient = -4×10^{-4} volts per degree. The effect of dilution on the e.m.f. is relatively small, showing that the activity coefficient of rubidium iodide in acetonitrile is considerably smaller than unity. The maximum solubility of rubidium iodide in acetonitrile is approximately 3%.[47]

Cryoscopic investigation of rubidium iodide in a nitrobenzene solution of aluminium bromide has shown that addition of rubidium iodide lowers the freezing point of the solution and that by increasing the addition of rubidium iodide in relation to aluminium bromide for a constant ratio of aluminium bromide to nitrobenzene, the partial depression of freezing point increases linearly.[48] Calculation of the apparent molecular weight of rubidium iodide corresponds to the theoretical molecular weight within experimental error. These regularities are due to the formation of molecular complexes which dissociate electrolytically as a binary electrolyte: $(AlBr_3I)Rb \rightleftharpoons (AlBr_3I)^- + Rb^+$.

In the system bismuth iodide–rubidium iodide–water, the isotherm at 12°C. has[49] 4 branches: (1) corresponding to the deposit of rubidium iodide, (2) to $3RbI,BiI_3$, (3) to $3RbI,2BiI_3$ and (4) to $BiI_3,3RbI$. $3RbI,2BiI_3$ forms bright red triclinic crystals. The solubility of bismuth iodide in solutions of rubidium iodide is approximately 24% at 12°C. In the system antimony tri-iodide–rubidium iodide–water[50] a solubility isotherm at 12°C. shows that SbI_3 is only slightly soluble even in concentrated solutions of RbI and it hydrolyzes in dilute solutions. The diagram has two branches corresponding (1) to the deposit of $SbI_3,1{\cdot}5RbI$ and (2) to RbI. $SbI_3,1{\cdot}5RbI$ is triclinic and forms clear, slightly orange-red almost rhombic prisms. Residues containing a mixture of the double salt and rubidium iodide, when left to evaporate undisturbed for a sufficient length of time, deposit small dark red, almost black tetragonal crystals analogous in form to $BiI_3,3RbI$. Points representing the composition of the liquor from which they form occur in the diagram near the zone corresponding to the salt $BiI_3,3RbI$ and they are therefore identified as being probably $SbI_3,3RbI$.

In the system mercuric iodide–rubidium iodide–water,[51] application of Schreinemaker's method of residues at 34°C. proves the existence of the double salts HgI_2,RbI,H_2O and $3HgI_2,5RbI$ only. Neither $HgI_2,2RbI$ nor HgI_2,RbI was found at this temperature.

Table VI[52] gives freezing point, solubility and boiling point data for the system rubidium iodide–water. The phase diagram based on these data, given in Fig. 1, shows a eutectic at −13·0°C. and that the boiling point of the saturated solution is 116·4°C. at 760 mm.

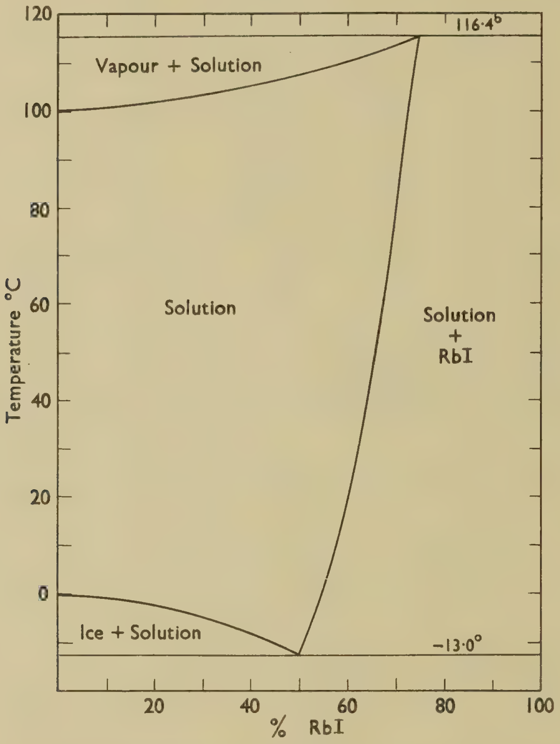

FIG. 1.- THE SYSTEM RUBIDIUM IODIDE–WATER AT 760 m.m.

TABLE VI.- DATA FOR THE SYSTEM RUBIDIUM IODIDE–WATER.

Soln. + Ice		Soln. + Vapour		Soln. + RbI		Soln. + RbI	
Temp.	%RbI	Temp.	%RbI	Temp.	%RbI	Temp.	%RbI
−1·3	9·58	101·1	15·56	−10	51·18	25·0	62·0
−3·5	20·13	102·4	30·79	−2·7	54·51	25·0	61·93
−6·2	31·33	104·6	46·04	0	55·5	25·6	62·9
−8·4	38·43	108·8	60·93	3·2	57·05	35·6	64·7
−8·6	39·15	110·7	65·58	6·9	57·9	48·5	66·76
−12·2	48·11	113·8	71·57	13·9	60·2	59·4	68·61
−13·0*E*	49·79	116·3	75·7*t*	17·4	60·3	77·2	70·89
−13·0*E*	50·11	116·4*S*	76·0*t*	18·0	59·0	93·0	73·01
		116·4*S*	77·8*t*	24·3	63·66	111·5	75·05

E = eutectic; *S* = saturated with solid phase;
t = total composition (solid and liquid).

Chemical Properties

A double salt RbI,$MgSO_4$ of the type KCl,$MgSO_4$, has been obtained.[53] The electrical conductivity of the fused kainite system has a sharp minimum at the molar ratio 1:1, thus indicating a decrease in the number of ions, *i.e.* persistance of the complex ions characteristic of kainite even in the fused state. The electrolytic dissociation is probably $RbI,MgSO_4 \rightleftharpoons Rb^+ + [IMgSO_4]^-$. The formation of the salt is thus contingent on the relative attractions of Rb^+ and Mg^{++} for I^- and is determined by the generalized moment $\mu = Z/r$ where Z = charge and r = radius of the ion.

The preparation of the following complex iodides has been claimed:[54] SnI_6Rb_2, SnI_3Rb, Sn_2I_5Rb, $2SnI_2,RbI$ and $[SnBr_{4.81}I_{1.19}]Rb_2$. Attempts to prepare a titanium iodide of rubidium gave a residue of RbI_3 and $Ti(OH)_3I,2H_2O$.

Rubidium iodide reacts with sulphamic acid, $HSO_3.NH_2$, to give the tri-iodide.[55]

The stability of rubidium iodide sulphone, $RbI,3SO_2$, is indicated by the following dissociation tensions: at −22·5–8°C., 52 mm.; 0°C., 278·25 mm.; 15·4°C., 765 mm.; 15·5°C., 760 mm. Additional experimental evidence of the sulphone is given by the pressure *vs.* weight of SO_2 curve.[56] The compound is canary yellow in colour, its heat of evaporation is 10·5 kg.-cal./mol. and decomposition temperature 15·3°C., in good agreement with earlier data.[57]

If rubidium iodide is substituted for potassium iodide in the preparation of Nessler's solution, the resulting reagent is extremely sensitive.[58]

RUBIDIUM POLYIODIDES

Investigation of the system rubidium iodide–iodine by Briggs and Patterson from 60°C. up to 238°C., the boiling point of the saturated melt, showed the solid phases in contact with the melt to be iodine, rubidium iodide and rubidium tri-iodide. The tri-iodide melted incongruently at 188°C. and a eutectic mixture contained 17·4 mol.-% of rubidium iodide and melted at 80·8°C. There was no evidence of the formation of higher polyiodides.[59] From thermal analysis of the system, Fialkov and Kuz'menko subsequently deduced that polyiodides are not formed when rubidium iodide is fused with iodine, indicating that the presence of a solvent is essential for their formation.[60] Further work by Briggs and co-workers,[61] however, indicates that the system has a eutectic point (iodine–rubidium tri-iodide) at 80·8°C. and 15·1% of rubidium iodide, a transition point (rubidium tri-iodide–rubidium iodide) at 188°C. and 40·6% of rubidium iodide and a saturated boiling point (melt, rubidium iodide, vapour) at 238°C. (740–750 m.m.) and 41·8% of rubidium iodide. Measurement of the electric conductivity of rubidium iodide in iodine between 130°C. and 140°C. shows[62] that the specific conductivity increases with concentration of the iodide and reaches a maximum of $2{\cdot}4 \times 10^{-1}$ at 130°C. The molar conductivity reaches a maximum of 139·3 at 4·36% RbI and then decreases with further increase of iodide concentration. The temperature coefficient of the specific conductivity is negligible at small concentrations of iodide and becomes positive at higher concentrations. The electric conductivity of iodide solutions in iodine is said to be conditioned by the polymerisation of polyiodides, the polymers dissociating electrolytically: $(RbI_3)_2 \rightleftharpoons Rb^+ + RbI_6^-$, or $(RbI_3)_2 \rightleftharpoons I^- + Rb_2I_5^+$. Comparison of the specific and molar conductivities of the rubidium iodide–iodine system with those of the potassium iodide–iodine and tetramethylammonium iodide–iodine systems shows considerable similarity in the conductivity isotherms and in respect to variations with concentration and temperature.[63]

Fig. 2 shows a phase diagram for the system rubidium iodide–iodine–water. The solid phases are ice, rubidium iodide, rubidium tri-iodide and iodine. There are no higher polyiodides and no hydrated tri-iodides. There is only one ternary eutectic (*i.e.* point *B*, ice–rubidium iodide–rubidium tri-

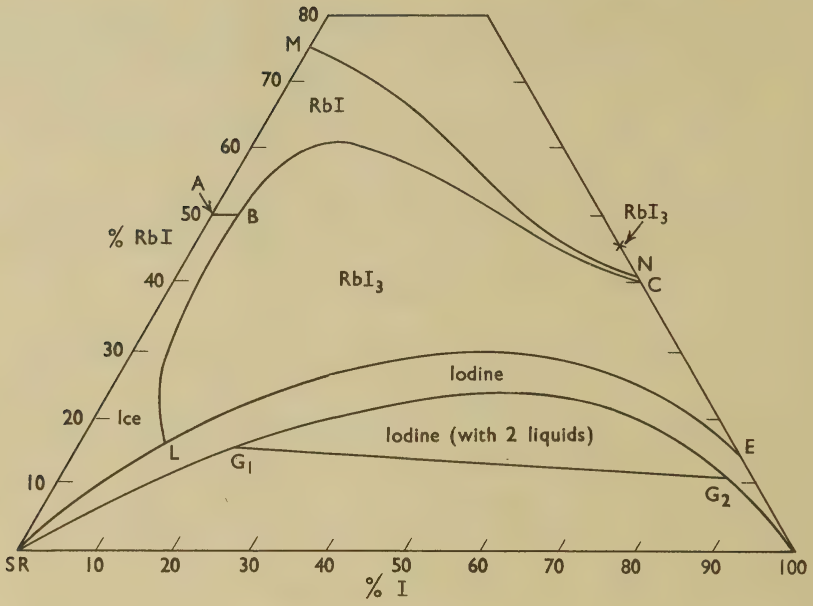

FIG. 2.- DIAGRAM OF RUBIDIUM IODIDE–IODINE–WATER AT 740–750m.m.

iodide) and no dystectics. The binary and ternary invariants of the system, with temperatures, percentage compositions and phases present are given in Table VII.

TABLE VII.- BINARY AND TERNARY INVARIANT POINTS IN THE SYSTEM RUBIDIUM IODIDE–IODINE–WATER.

Position	Temp. °C.	Liquid		Phases present
		%I	%RbI	
S	0 *E*	Trace	0	Ice, iodine, liquid
A	−13 *E*	0	49·9	Ice, RbI, liquid
E	80·8 *E*	84·9	15·1	RbI_3, iodine, liquid
C	188 *U*	59·4	40·6	RbI_3, RbI, liquid
R	98·2 *B*	0·4	0	Iodine, liquid, vapour
H	113 *B*	99·9	0	Iodine, liquid, vapour
M	116 *B*	0	75·5	RbI, liquid, vapour
N	238 *B*	58·2	41·8	RbI, liquid, vapour
B	−13·9 *E*	1·6	50·1	Ice, RbI, RbI_3, liquid
L	−2·6 *U*	13·0	16·9	Ice, RbI_3, iodine, liquid
G_1	98·4 *B*	21·5	15·3	Ice, 2 liquids, vapour
G_2	98·4 *B*	83·4	10·9	Ice, 2 liquids, vapour

E = Eutectic point; *U* = transition point; *B* = boiling point (740–750 mm.)

The tri-iodide melts incongruently at point *C* (188°C.) where it decomposes into a binary liquid and solid rubidium iodide. The tri-iodide is isothermally congruently soluble in water between 7·8°C. and 132°C. Crystallisation paths converge sharply at point *X* (54·45% iodine, 45·55% rubidium iodide) corresponding to rubidium tri-iodide, thus verifying its existence.[64]

Solubility determinations in the systems rubidium iodide–iodine–toluene and rubidium iodide–iodine–benzene at 6°C. and 25°C. show[65] that at each temperature there are one binary compound RbI_3 and two ternary compounds $RbI,6I,4C_6H_6$ and $RbI,7I,4C_6H_6$. These compositions for the ternary compounds differ from those of Grace who reported $RbI_9,2C_6H_6$ and $RbI_7,2C_6H_6$. The same author gave the dissociation pressure of the tri-iodide = 0·00101 m.m. at 6°C. and 0·00736 m.m. at 25°C. and heat of dissociation = −17·2 kg.-cal. The heat of dissociation is greater than that of cæsium tri-iodide.[66]

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SECTION LXXII

RUBIDIUM SULPHIDES

By L. F. WILSON

Rubidium monosulphide, Rb_2S, is readily prepared by direct combination of the elements in vacuo. A modification of this method employs mercuric sulphide in place of sulphur and has the advantage that polysulphide formation is avoided.[1]

$$2Rb + HgS \rightarrow Rb_2S + Hg$$

An excess of rubidium metal is used over the quantity required to give Rb_2S; the excess metal, and the mercury formed by the reaction, are distilled off in vacuo. The monosulphide may also be prepared by reaction between the calculated quantities of rubidium and sulphur in liquid ammonia solution.[2] The reduction of rubidium sulphate by hydrogen or ammonia at high temperatures also produces rubidium monosulphide,[3] although this method may give a product contaminated with rubidium pyrosulphate.[4]

Rubidium monosulphide is colourless at room temperature but darkens to an orange colour at 500°C. The melting point is 530°C. and at this temperature thermal decomposition takes place.[1] The compound is diamagnetic and the magnetic susceptibility is $-0{\cdot}38 \times 10^{-6}$ and $-0{\cdot}39 \times 10^{-6}$ at -183°C. and 20°C. respectively.[2] The crystal structure is of the fluorite type and the lattice constant has been reported as 7·35 A.[5] and 7·65 A.[6]

Rubidium hydrosulphide, RbSH, is made by passing hydrogen sulphide through a solution of rubidium hydroxide. It is also formed as a white powder when hydrogen sulphide is passed over rubidium metal powder protected from the atmosphere by an inert liquid such as toluene.[6] Rubidium hydrosulphide crystallises in the rhombohedral system and the unit cell dimensions[6] are $a = 4{\cdot}53$ A. and $\alpha = 69^\circ\ 20'$. A high temperature form has the fluorite structure, $a = 6{\cdot}93$ A.

Rubidium forms several *polysulphides* and compounds up to Rb_2S_6 have been reported. The colours of these polysulphides and values of their magnetic susceptibility at -183°C. and 20°C. are given below.

	Colour	χ (−183°C.)	χ (20°C.)
Rb_2S_2	Yellow	$-0{\cdot}38 \times 10^{-6}$	$-0{\cdot}39 \times 10^{-6}$
Rb_2S_3	Red		$-0{\cdot}38 \times 10^{-6}$
Rb_2S_4	Red-brown	$-0{\cdot}36 \times 10^{-6}$	$-0{\cdot}37 \times 10^{-6}$
Rb_2S_5	Brown	$-0{\cdot}35 \times 10^{-6}$	$-0{\cdot}37 \times 10^{-6}$
Rb_2S_6		$-0{\cdot}36 \times 10^{-6}$	$-0{\cdot}36 \times 10^{-6}$

The reaction in liquid ammonia between rubidium polysulphide and rubidium metal has been studied by potentiometric methods.[7] The polysulphide was prepared by reaction between rubidium metal in liquid ammonia and enough sulphur to give the composition Rb_2S_x with $x > 6$. The polysulphide forms very slowly and gives a red solution with liquid ammonia. A graph showing the potentiometric titration of the polysulphide solution with rubidium metal is given in Fig. 1. The results indicate the successive formation of rubidium tetrasulphide, Rb_2S_4, and rubidium disulphide, Rb_2S_2. The yellow crystals of the disulphide react only very slowly with the metal solution and it is not practical to continue the titration to the monosulphide end-point.

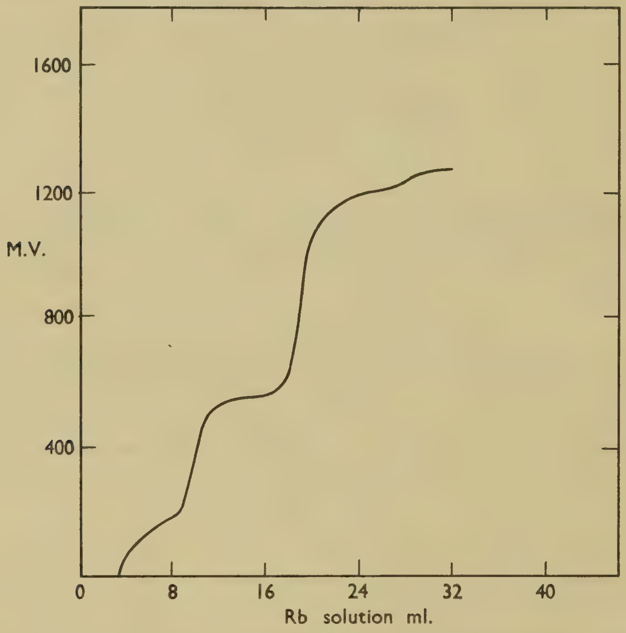

FIG. 1.- TITRATION OF RUBIDIUM POLYSULPHIDE WITH RUBIDIUM

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SECTION LXXIII

RUBIDIUM SULPHATE

By N. M. HOPKIN

Meerov[1] obtained a 98·2–100% yield when preparing rubidium acid sulphate by evaporating the pyrosulphate over phosphorus pentoxide. The sulphate had m.p. 285°C. and began to decompose between 170° and 200°C. If it was melted rapidly there was no apparent decomposition. On the other hand Duval[2] reported that whereas rubidium sulphate is stable between 76° and 877°C., the acid sulphate must be heated above 880°C. to obtain complete decomposition. The temperatures at which the normal sulphate begins to be reduced[3] in streams of hydrogen and ammonia were found by Spitsyn *et al.* to be 670° and 790°C. respectively. Table I shows the loss by volatilisation found by these authors when rubidium sulphate is heated under various conditions from 800° to 1200°C. No chemical decomposition was detected.

TABLE I.- VOLATILISATION OF RUBIDIUM SULPHATE

Temp. °C.	Volatilisation loss per hr.
800 (in still air)	none
900 (in still air)	0·08%
1000 (in still air)	0·27%
1200 (in still air)	3·14%
1200 (in a stream of water vapour: 18 g./hr.)	40·44%

The alkali metal sulphates with the highest m.p. have also the highest volatilities. The volatilities of potassium, rubidium and cæsium sulphates are in the ratio of 1:1·4:2·1. They differ more than one would expect from the closeness of their m.p., which are 1074°, 1074° and 1019°C. respectively. Volatility may be determined by the changes of bonding which take place in the liquid state rather than by the ionic bonding in the solid state. The stronger the bonding in the solid state the more it appears to give rise to a weaker bonding when liquid. Spitsyn attributes the increase in volatility from sodium sulphate to rubidium sulphate to the polarization of the cation by the oxygen atoms of the sulphate ion and the corresponding shift from the ionic to the polar bond.

A study of the diffusion of alkali salt vapours in the Bunsen flame[4] gave the coefficient of diffusion of rubidium sulphate as 11·7 ± 10%, the flame temperature being 1436°C. as measured by Fery's method. The metal atoms would seem to be free during part of the time of diffusion. The diffusion coefficients of the sulphate in aqueous solution of normality 0·1, 0·25 and 0·5 at 20°C. are reported by Öholm[4] as 1·027, 0·985 and 0·968 respectively.

Table II gives the activity coefficients (γ) and osmotic coefficients (ϕ) derived by Stokes[4] chiefly from isopiestic vapour pressure determinations for 1:2 salts of the Na_2SO_4 type at 25°C. These figures agree very well with those determined experimentally by Cudd and Felsing[4] for these compounds, and their accuracy is probably in the range 1 in 200 to 1 in 500.

TABLE II.- OSMOTIC AND ACTIVITY COEFFICIENTS OF RUBIDIUM AND CAESIUM SULPHATES IN AQUEOUS SOLUTION AT 25°C.

	Rb_2SO_4		Cs_2SO_4	
M.	ϕ	γ	ϕ	γ
0·1	0·799	0·452	0·804	0·456
0·2	0·764	0·373	0·772	0·380
0·3	0·740	0·331	0·751	0·339
0·4	0·724	0·302	0·739	0·312
0·5	0·714	0·281	0·731	0·292
0·6	0·705	0·264	0·725	0·276
0·7	0·698	0·261	0·721	0·263
0·8	0·691	0·241	0·717	0·253
0·9	0·686	0·229	0·714	0·244
1·0	0·681	0·221	0·712	0·237
1·2	0·677	0·207	0·711	0·223
1·4	0·677	0·197	0·713	0·215
1·6	0·679	0·191	0·716	0·210
1·8	0·684	0·187	0·722	0·206

The main factor controlling the behaviour of these electrolytes is the size of their ions and its effect on the extent of cation hydration. The K^+ ion is too large to hydrate at all firmly and the order of decreasing activity of the alkali metal ions is found to be: $Li^+ > Cs^+ > Rb^+ > Na^+ > K^+$. The corresponding crystallographic radii are 0·6:1·69:1·48:0·95 and 1·33 A., respectively. But if allowance is made for the considerable degree of hydration of Li^+ and the slightly hydrated Na^+, the order of the ionic radii will correspond to the order of their activity coefficients. The acid function of an aqueous solution is directly proportional to the ionic strength when no complex ion is formed, but when rubidium sulphate is added to 0·943 M. sulphuric acid Flid and Moiseev[4] found that the acid function of the solution decreases with increasing concentration of the sulphate, despite the increase in ionic strength. The effect becomes more marked in the order lithium, sodium, ammonium, potassium, rubidium, which is also the order of increasing ionic radii and activities.

The binary system rubidium sulphate–magnesium sulphate has been studied thermographically[5] and it is found that a eutectic is formed at 675°C. containing 47·5 mol.-% of $MgSO_4$. The formation of the compound $Rb_2SO_4,2MgSO_4$ was indicated by an inflexion of the cooling curve at 59 mol.-% $MgSO_4$ at 850°C. The existence of this compound was also confirmed by *X*-ray analysis.

An investigation of double sulphates of the rare earth and alkali metals revealed a double salt of neodymium and rubidium sulphate stable at 25°C.; its formula was $Nd_2(SO_4)_3,Rb_2SO_4,8H_2O$ and it had a wide range of existence in contact with solutions of neodymium and rubidium sulphates. It was stable in contact with solution containing from 4·73% Nd_2SO_4 and 1·2% to 45% Rb_2SO_4, and isomorphous with the other corresponding rare earth–ammonium sulphate double salts and with $Nd_2SO_4,Tl_2SO_4,8H_2O$. The double salt $Ce_2(SO_4)_3,Rb_2SO_4,2H_2O$ also has a wide range of existence at 25°C. when in contact with solutions containing from 34% Rb_2SO_4 and no $Ce_2(SO_4)_3$ to solutions containing 1·3% Rb_2SO_4 and 0·2% $Ce_2(SO_4)_3$.

When solutions containing $Ce_2(SO_4)_3$ and Rb_2SO_4 in the molecular proportions 1:4 are evaporated at 10°C. the double salt $Ce_2(SO_4)_3,Rb_2SO_4,8H_2O$ is formed, while $Ce_2(SO_4)_3,Rb_2SO_4$ is obtained on evaporating at 30°C. when the two sulphates are present in the molecular proportions of 1:2. This is the first anhydrous double sulphate of a rare earth and alkali metal of this type to be prepared, and the temperature is critical for its formation.

Polytherms[7] have been determined for ternary systems containing water, manganous sulphate and rubidium sulphate. The solid phases found to be present are $Rb_2SO_4,MnSO_4,6H_2O$, $2Rb_2SO_4,MnSO_4$ and the mono-, penta- and heptahydrates of manganous sulphate. These phases are shown in Fig. 1.

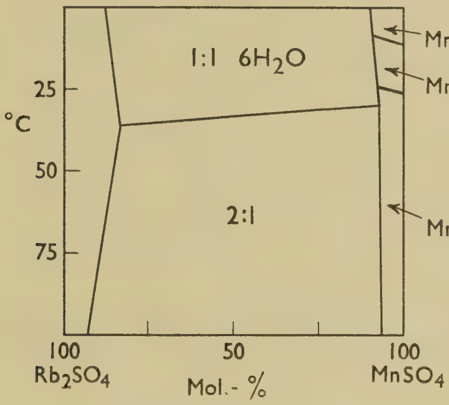


FIG. 1. POLYTHERMAL DIAGRAM OF THE SYSTEM $MnSO_4$–Rb_2SO_4–H_2O

over the temperature range of 0–100°C. The corresponding diagram for the systems Rb_2SO_4–$CoSO_4$–H_2O and Rb_2SO_4–$NiSO_4$–H_2O, also studied by Benrath, are of a similar type, as shown in Figs. 2 and 3, although here only one double salt was found in each case, both having six molecules of water. The molecular solubility of the double salt decreases with increasing atomic weight of the alkali metal, but the increase in solubility of the double salt with temperature indicates increasing decomposition into the components as the temperature rises. The nickel sulphate system is by far the simplest.

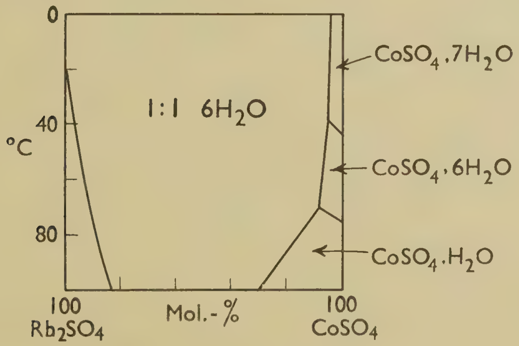


FIG. 2. POLYTHERMAL DIAGRAM OF THE SYSTEM Rb_2SO_4–$CoSO_4$–H_2O

The Rb_2SO_4–$CdSO_4$–H_2O system is the most complex, yielding four double salts, shown in Fig. 4 and labelled *Sch* ($Rb_2SO_4,CdSO_4,6H_2O$), *C* ($Rb_2SO_4,CdSO_4,2H_2O$), *D* ($Rb_2SO_4,3CdSO_4,5H_2O$) and *L* ($Rb_2SO_4,2CdSO_4$).

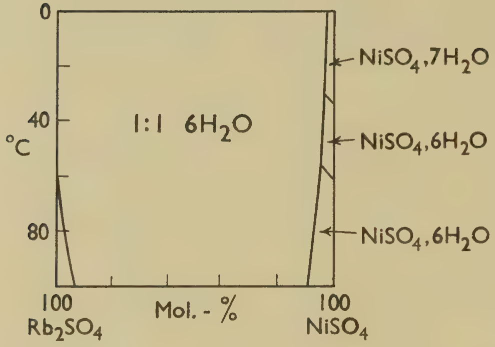


FIG. 3. POLYTHERMAL DIAGRAM OF THE SYSTEM Rb_2SO_4–$NiSO_4$–H_2O

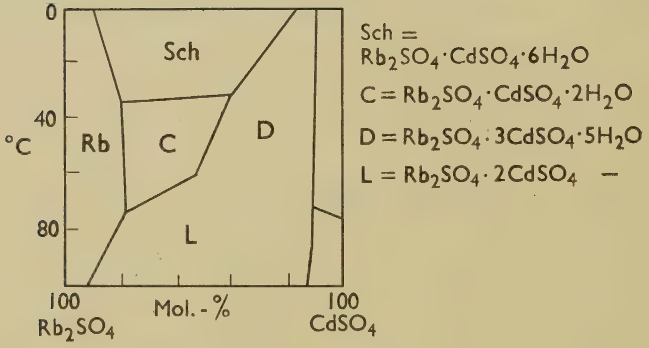
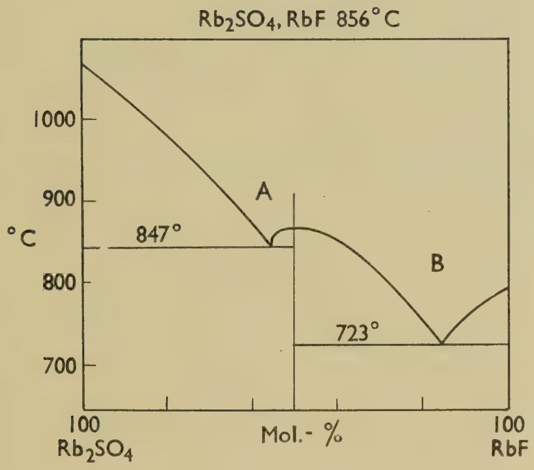

0
40
°C
80
Sch
Rb
C
D
L
100
Rb_2SO_4
Mol. - %
100
$CdSO_4$
Sch =
$Rb_2SO_4 \cdot CdSO_4 \cdot 6H_2O$
C = $Rb_2SO_4 \cdot CdSO_4 \cdot 2H_2O$
D = $Rb_2SO_4 \cdot 3CdSO_4 \cdot 5H_2O$
L = $Rb_2SO_4 \cdot 2CdSO_4$

FIG. 4. POLYTHERMAL DIAGRAM OF THE SYSTEM Rb_2SO_4–$CdSO_4$–H_2O

In the system Rb_2SO_4–Ag_2SO_4–H_2O the only solid phases are the pure salts.[8] The isothermally invariant solution which is saturated with the two salts has the following composition at 25°C.: 1·38% Ag_2SO_4, 33·63% Rb_2SO_4. Its density, 1·372, was determined from a study of the solubility measurements by making the complex in a sealed tube and waiting for two days to ensure complete equilibrium.

In the phase diagram of the system Rb_2SO_4–RbF there are two eutectic points[9] corresponding to rubidium fluoride contents of 43% and 86% respectively as shown in Fig. 5.

When present in 0·1 M. copper sulphate solutions during the electrodeposition of copper, rubidium sulphate, in amounts up to 0·4 M. hinders the



Eutectic A = 43% RbF
Eutectic B = 86% RbF

FIG. 5. EQUILIBRIUM DIAGRAM OF THE SYSTEM Rb_2SO_4-RbF

access of cupric ions to the cathode.[10] The depressing effect of this phase polarisation increases in the order lithium < sodium < potassium < rubidium < caesium.

Rubidium sulphate has been used to stabilise a hydrogenation catalyst such as nickel, metallic copper and chromic oxide, the alkali metal sulphate being present in the proportion of 2 parts per 100 parts of nickel with the total alkali metal sulphate content being less than 0·33 gram-molecules per gram-atom of nickel.

In a study of the chemotherapy of typhus[11] no appreciable activity of rubidium sulphate was found against typhus in guinea pig or mouse experiments: also over a wide range of concentration rubidium sulphate did not affect the germination or the growth of barley, wheat, oats, peas or beans in nutrient solutions.

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SECTION LXXIV

RUBIDIUM CARBONATE

By N. M. HOPKIN

Physical Properties

The dielectric constant of rubidium carbonate has been determined by Schupp[1] and found to be 6·73 (wave-length 1800 m. at 18°C.). The use of powder or fused salt does not give very reliable results. Schupp devised a method whereby the powdered salt is added to a liquid placed between the plates of a condenser and the liquid is changed until one is found the total capacity of which does not change with additions of the salt. Then the dielectric constant of the salt is that of the liquid used.

Four- and five-liquid equilibrium systems have been reported by Carrière[2] of which one of the phases can be a saturated solution of rubidium carbonate. In the case of the four-liquid system the other three liquids can be saturated aqueous ammonia, a saturated aqueous solution of sodium oleate, and aniline, hexane, nitrobenzene, neutral peanut (or olive) oil or castor oil. An example of a five-liquid equilibrium system is saturated rubidium carbonate, saturated aqueous ammonia, concentrated sodium oleate solution, hexane and aniline. The sodium oleate phase decreases in volume with increasing temperature and disappears altogether at 26°C.

In order to study the trends of the thermal effects Q (kg.-cal./mole) of reciprocal systems formed by a pair of alkali metals and of anions Diogenov[3] has devised a classification system in which lithium–sodium, lithium–potassium, lithium–rubidium, lithium–caesium constitute Group I. Group II comprises sodium–potassium etc. making four groups in all. Taking each Group separately, and independently of the nature of the anion pair, the systems are invariably irreversibly reciprocal, and for any given pair of cations and one fixed anion the shift of equilibrium is always the greater the smaller is the radius of the other anion of the pair. Taking one fixed cation (rubidium) for the system containing hydroxyl and carbonate anions, Q will increase with increasing atomic weight of the other cation. See Table I.

TABLE I.- THERMAL EFFECTS OF ALKALI METAL PAIRS WITH OH^- AND $CO_3^=$ ANIONS

Alkali Metal Pairs	Q kg.-cal./mole
Li, Rb	0·4
Na, Rb	2·5
K, Rb	6·8
Cs, Rb	7·1

The equilibrium phase diagram for the binary mixtures of rubidium carbonate and rubidium fluoride given by Schmitz-Dumont and Heckman,[4] shows the existence of two eutectics (Fig. 1.), one melting at 627°C. and containing 51% of the carbonate and the other melting at 616°C. with 34% of carbonate. There is also a maximum on the liquidus curve corresponding to the mixture Rb_2CO_3–RbF.

Refs. p. 2247

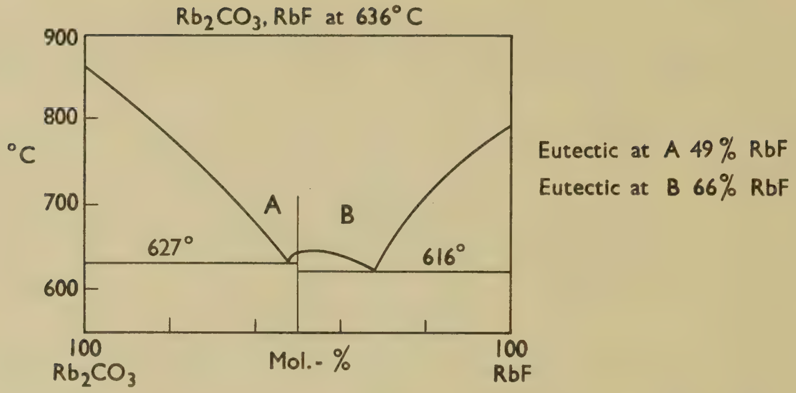

FIG. 1. EQUILIBRIUM DIAGRAM OF RUBIDIUM CARBONATE AND RUBIDIUM FLUORIDE

Reactions and Chemical Properties

When anhydrous neutral rubidium carbonate[5] is added to an aqueous solution of ammonia of any concentration and the temperature of the mixture is maintained below 20°C., two layers form at saturation point. The upper layer contains 99% of the ammonia and the lower layer 99% of the carbonate. These layers are stable in the presence of potassium hydroxide and orthophosphoric acid, but they become completely miscible on dilution or when heated above 60°C. Copper acetate added to this system dissolves and becomes concentrated in the lower, carbonate, layer and only traces of copper are found in the upper layer. If the carbonate layer is not saturated the addition of the copper salt will cause the layers to coalesce. But on the addition of more carbonate to the point of saturation, the two components will again separate, with the copper in the lower layer of the system.

Rubidium carbonate[6] can be formed by the thermal decomposition of rubidium formate below 400°C., but at this temperature in the presence of condensation catalysts and *in vacuo* rubidium oxalate will form. In the presence of metallic sodium the decomposition product contains 66·8% of rubidium oxalate, even at 300°C. In his study of the hydrolysis of the alkali metal carbonates Guiter[7] has found the following figures, taking the hydrolysis reaction in four stages.

(I) At about 1 N., $\Delta pH = 0{\cdot}05$,

$$(CO_3^{--})_3 + 3H_2O \rightleftharpoons 3CO_3H^- + 3OH^-$$

The hydrolysis constant = $3{\cdot}32 \times 10^{-13}$ and the extent of hydrolysis varies from 0·5% to 5·0%.

(Ia) At about 0·1 N. there is a different reaction to the same point of the hydrolysis curve and $\Delta pH = 0{\cdot}3$:

$$CO_3^{--} + M^+ + H_2O \rightleftharpoons CO_3HM + OH^-$$

The hydrolysis constant here is $1{\cdot}25 \times 10^{-3}$ and equilibrium is reached at about 5% hydrolysis.

(II) At about 0·01 N., $\Delta pH = 0{\cdot}2$ and the reaction becomes:

$$2CO_3^{--} + 2H_2O \rightleftharpoons (CO_3H^-)_2 + 2OH^-$$

The hydrolysis constant is $2{\cdot}23 \times 10^{-6}$ and the hydrolysis increases from 5 to

15%.

(III) At about 0·001 N., ΔpH = 0·75:

$$CO_3^{--} + 4M^+ + H_2O \rightleftharpoons (CO_3M_4H)^{+++} + OH^-$$

The hydrolysis constant is $4{\cdot}4 \times 10^{-5}$ and the hydrolysis decreases from 15 to 0·2%.

(IV) At about 0·0001 N., ΔpH = 0·15:

$$CO_3^{--} + H_2O \rightleftharpoons CO_3H^- + OH^-$$

The hydrolysis constant is $4{\cdot}5 \times 10^{-10}$ and the hydrolysis increases again from 0·2% to 0·5%. The hydrolysis reactions are identical for sodium, potassium and lithium as well as for rubidium and cæsium when the metals do not enter into the reaction. In a 0·001 N. solution cation complexes appear the structures of which point to the existence of steric hindrance. The order of reactivity[8] of titanium oxide with the alkali carbonates decreases in the order: cæsium (decomp. 610°C.), lithium (m.p. 732°C.), rubidium (m.p. 837°C.), sodium (m.p. 852°C.) and potassium (m.p. 891°C.), the order of their melting points.

While studying the thermodynamic properties of carbonates in order to elucidate their behaviour in metallurgical processes Kelley and Anderson[9] have assembled what data there are on rubidium carbonate and bicarbonate. For the bicarbonate Caven and Sand[10] assumed the changes in specific heat during the decomposition reaction between 285° and 444° K. to be the same as those of sodium bicarbonate. The results of determinations of the heat and free energy of decomposition were affected by moisture in the samples at temperatures below 373° K.

$$\Delta c_p = 9{\cdot}15 - 25{\cdot}5 \times 10^{-3}T$$

$$2RbHCO_3 \rightarrow Rb_2CO_3 + CO_2 + H_2O\ (g)$$

$$\Delta H = 34{,}580 + 9{\cdot}15T - 12{\cdot}75 \times 10^{-3}T^2$$

$$\Delta F^\circ = 34{,}580 - 21{\cdot}07T \log T + 12{\cdot}75 \times 10^{-3}T^2 - 26{\cdot}28T$$

$$\Delta H_{298\cdot1} = 36{,}180$$

$$\Delta F^\circ_{298\cdot1} = 12{\cdot}340$$

$$\Delta S_{298\cdot1} = 80{\cdot}0$$

No calculation was made for rubidium carbonate because of lack of data. The thermal value, given by De Forcrand,[11] of $\Delta H_{298} = 97{,}420$ for the reaction:

$$Rb_2CO_3 \rightarrow Rb_2O + CO_2$$

and the decomposition pressure, determined by Lebeau[12] at 1013–1353°C., apply to the liquid state. The melting point is 837°C.

Applications

Rubidium carbonate, when used as a condensing agent[13] in the transformation of *o*-aroyloxyacetarones into *o*-hydroxydiaroylmethanes, gives a yield of 82%. The carbonate has also been used as a catalyst[14] for the copolymerization of 2,5-oxazolidinediones such as 4-*iso*butyl- and 4-dimethyl-2,5-oxazolidinediones.

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SECTION LXXV

RUBIDIUM NITRATE

By N.M. HOPKIN

In the fused state rubidium and cadmium nitrates react together to form a double salt[1] of the composition $Cd(NO_3)_2,2RbNO_3$ which melts at 184°C. and is less stable thermally than the isomorphous double salt of cadmium and potassium nitrate, $Cd(NO_3)_2,2KNO_3$. The liquidus surface of the system rubidium–cadmium–potassium nitrate shows that these two compounds are formed in the crystallisation field within the ternary system. In aqueous solutions the tendency to form complexes with lead nitrate increases with the atomic number of the alkali metal. The existence of compounds of the composition[2] $Pb(NO_3)_2$,-$RbNO_3$, $Pb(NO_3)_2,2RbNO_3$ and $Pb(NO_3)_2,4RbNO_3$ has been established by viscosity and conductivity measurements. A compound of one molecule of rubidium nitrate and one molecule of thorium nitrate exists in aqueous solution; but in the solid state[3] an anhydrous compound with two molecules of rubidium nitrate has been isolated. The magnetic susceptibility $[\chi_M]$ for this latter compound[4] has been determined $[\chi_M = -154{\cdot}9 \times 10^{-6}]$, but this differs from the calculated value, $-202{\cdot}8 \times 10^{-6}$, which indicates that there is some modification in the molecular structure. The thorium nitrate molecule is most strongly attached to the rubidium nitrate and the diamagnetism of the two constituents falls. The influence of cation radius and salt concentration upon the salting out of ethyl ether from aqueous nitrate solutions has been studied by Heal.[5] Table I shows the solubility of ethyl ether in aqueous rubidium nitrate solutions, where the probable error for low values of m is ±0·03%. The best equation to describe the effect of salt concentration is $\log S_0/S = km$, where S_0 and S are the molal solubilities of ethyl ether in pure water and in solution of salt of molality m respectively. At high concentration the salting out is less than is predicted by the equation. The solubility (S_0) of ethyl ether in water was found to be 0·8599 molal. The effect of cation radii was again in the same direction as found for lead nitrate at low dilutions.

TABLE I.- MOLAL SOLUBILITIES OF ETHYL ETHER IN AQUEOUS RUBIDIUM NITRATE AT 25°C.

Solubility of Et_2O molality	Concentration of $RbNO_3$ molality
0·8526	0·0250
0·8478	0·0487
0·8341	0·1012
0·8231	0·1484

The low melting points of the alkali metal nitrates as compared with their halides (rubidium nitrate has m.p. = 305°C.)[6] has been attributed to the formation of association complexes in the nitrate melts which would contribute a term to the over-all entropy of melting without much increasing the heat of fusion. The small volume changes on fusion of the melts and the abnormal activation energy for their viscosities support this type of mechanism of melting. The transition of the crystal lattice from a cubic to a trigonal form together with the rotation of the nitrate ion takes place[7] at 250°C.

The cubic structure of the nitrate has been investigated by Korhonen[8] using a Wasastjerna focusing camera. The nitrate samples were in the form of briquettes maintained at 190°C. The cubic unit cell suggested by Finbak[7] with $a = 4{\cdot}37$ A. proved to be too small for structures containing fixed or rotating nitrate ions. An axial length $a = 8{\cdot}74$ A. was favoured and this larger cell was to some extent verified by the existence on a strongly exposed photograph of five weak reflections between those formerly designated as (211) and (220). The space group was found to be $T_h^6 - Pa^3$ and the position of the atoms was given as 8 atoms of rubidium at the corners of the cell, at its centre and the centres of the edges of the cell; 8 nitrogen atoms on the body diagonals of the cell at *uuu* [$u = 0{\cdot}285$]; and 24 oxygen atoms at *xyz* [= 0·278, 0·278 and 0·399 respectively]. This new size for the nitrate cell differs from the two structures previously reported by Pauling.[9]

These were a pseudo-hexagonal cell with the dimensions $a = 10{\cdot}45$ A. and $c = 7{\cdot}38$ A., containing 9 molecules, and an orthorhombic cell derived from Laue data with $a = 18{\cdot}08$ A., $b = 10{\cdot}45$ A. and $c = 7{\cdot}38$ A. containing 18 molecules.

An interesting method of differential thermal analysis has been used by Gordon[10] *et al.* to determine the melting points and temperatures of crystalline transitions. This method measures the temperature difference between an inert reference compound, such as ignited alumina, and the sample to be investigated, when they are heated together at a constant rate in the same furnace. The reference compound chosen is one which will not undergo any thermal reactions over the temperature range to be used. Therefore any exo- or endothermic changes in the sample will cause its temperature to be higher or lower, respectively, than that of the reference material. These exo- or endo-thermic differentials can be recorded as a function of the temperature of the sample or of the furnace. This method has given the melting point of the nitrate as 249°C. The compound bubbles slightly at 609°C., rapidly at 642°C., and vigorously at 881°C. Rubidium nitrate is the only alkali metal nitrate to undergo two crystalline transitions. These are hexagonal $\xrightarrow{167^\circ\text{C.}}$ cubic $\xrightarrow{221^\circ\text{C.}}$ rhombic.

Hydrazine[11] forms a eutectic mixture with 22% of rubidium nitrate; it freezes at 36°C. There is no evidence that any double salts are formed.

Rostkovskii[12] has established that there are four polymorphous forms of rubidium nitrate in existence between room temperature and its melting point; the transition temperatures are 164–6°C., 222–8°C. and 290–2°C. His phase diagram for the binary system of rubidium nitrate and chloride shows the existence of two complexes. One of these contains 10·4 mol.-% of the nitrate at 340°C. and the other 24 mol.-% of the nitrate at 394°C. Blidin[13] has also investigated this system, when studying the reciprocal system of rubidium and cæsium chlorides and nitrates. Rubidium and cæsium nitrates form a continuous series of solid solutions with a minimum m.p. at 290°C. In the binary system of rubidium and lithium nitrates (Fig. 1) a compound of composition corresponding to $RbNO_3,LiNO_3$[13,14] melts at 191°C.; it forms solid solutions with either salt. There are also eutectics of the two salts at 179·5°C. and 154°C., corresponding respectively to 35 and 68 mol.-% of rubidium nitrate. The rubidium–potassium nitrate system forms a series of continuous solid solutions with a minimum m.p. about 292°C. at a composition of 67 mol.-% of rubidium nitrate. The eutectic mixture of rubidium nitrate and sodium nitrate contains 55 mol.-% of the former and melts at 178·5°C. (Fig. 2). Ternary mixtures[15] of

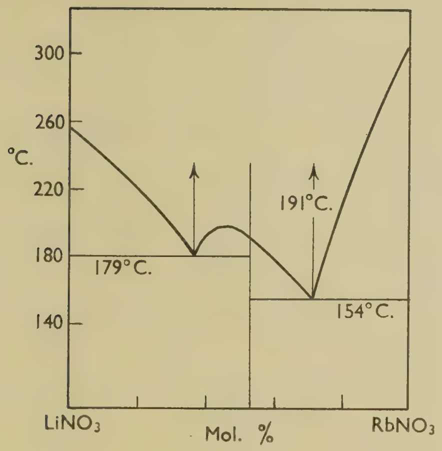

FIG. 1.- EQUILIBRIUM PHASE DIAGRAM OF LITHIUM AND RUBIDIUM NITRATE

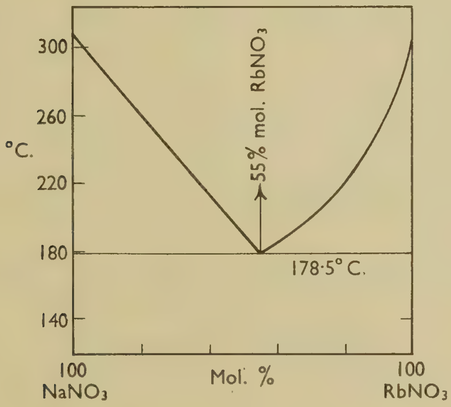

FIG. 2.- EQUILIBRIUM PHASE DIAGRAM OF SODIUM AND RUBIDIUM NITRATE

rubidium nitrate, caesium nitrate and calcium nitrate give minimum temperatures of fusion as shown in Table II. In the binary mixtures the existence of the compound $Ca(NO_3)_2,RbNO_3$, was confirmed.

When any two of these isomorphic compounds react chemically with the third compound then the resultant compounds are isomorphic. The shift of double decomposition in the mutually reversible system sodium chloride–rubidium chloride–sodium nitrate–rubidium nitrate[16] is towards the more stable couple, sodium chloride–rubidium nitrate. There are three eutectic points on the equilibrium diagram of this mixture:

(I) at 156°C. with 36·5 mol.-% $NaNO_3$
5·5 mol.-% NaCl
58 mol.-% $RbNO_3$

(II) at 210°C. with 10 mol.-% mRbNO$_3$,nRbCl
14 mol.-% NaCl
75·1 mol.-% RbNO$_3$

(III) at 330°C. with 29·5 mol.-% RbCl
23·6 mol.-% NaCl
46·9 mol.-% mRbNO$_3$,nRbCl

TABLE II.- MINIMUM MELTING POINT MIXTURES OF RUBIDIUM NITRATE, CÆSIUM NITRATE AND CALCIUM NITRATE

Molecular Percentage			Melting Point of mixture °C.
$RbNO_3$	$CsNO_3$	$Ca(NO_3)_2$	
59·0	2·2	38·8	128·0
35·3	6·5	58·2	112·5
53·0	9·5	37·5	130·0
45·5	16·5	38·0	130·0
41·0	20·5	38·5	132·0
28·0	32·5	39·5	145·0
14·0	44·5	41·5	168·0
5·0	52·4	42·6	176·0

Blidin conducted this study in test tubes, noting the appearance of the first crystals. The maximum temperature used was 500°C. and the melting point of rubidium nitrate was thus found to be 313°C. (see page 2249). Reciprocal systems with a pair of alkali-metal cations and the anion pair hydroxide and nitrate have been classified[17] into four groups with respect to the alkali metals. Thus Group 1 comprises metals adjacent in the periodic system, Group 2 comprises pairs of alternate alkali metals, Group 3 comprises the pairs Li–Rb and Na–Cs, whilst the fourth Group consists of the lithium–caesium pair. The thermal effects Q (kg.-cal./mole) of the exchange reactions of these systems are seen in Table III.

TABLE III.- THERMAL EFFECTS OF ALKALI METAL PAIRS WITH OH^- AND NO_3^- ANIONS

Alkali Metal Pairs	Q kg.-cal./mole
Li,Rb	2·0
Na,Rb	7·9
K,Rb	19·1
Cs,Rb	22·0

The thermal effect increases on descending Group I of the Periodic Table. The stable pairs of salts are always the hydroxide of the lighter metal with the nitrate of the heavier. Liquid layering is absent with the cation pairs potassium–rubidium and rubidium–caesium, but occurs with lithium–rubidium and sodium–rubidium. There is a tendency for compounds of the type MOH,-MNO$_3$ to occur in these systems where M is the same alkali metal. These can be considered as acid salts of orthonitric acid (H_3NO_4).

Like potassium nitrate, rubidium nitrate forms glasses with calcium nitrate using mixtures of 40–60% rubidium nitrate but the density, crystal velocity and viscosity of these melts have not been reported.[18]

Alkali metal ions have been studied in respect of their effect on the coagulation of colloidal solutions of sulphur. The amount a of the coagulating ion, expressed as a percentage of amount equivalent to sodium pentathionate

($Na_2S_5O_6$) required to stabilise the sol, is 37% for Rb^+. The coagulating concentration was in this case 0·10 g.- equivalent per litre of rubidium nitrate.[19]

The practical osmotic and activity coefficients of rubidium nitrate solutions over a large range of concentration have been determined by an isopiestic method[20] depending upon the difference in vapour pressure of two salt solutions. A small volume (2 ml.) of potassium chloride solution and the same volume of the salt solution to be studied are placed in two separate gold plated platinum dishes in a desiccator which is evacuated, maintained at 25°C. and rocked gently. Distillation occurs until both solutions have attained the same vapour pressure. Equilibrium is reached in 24hr. if the concentrations of the solutions are greater than 0·5 M. Changes in weight of the two solutions give the isopiestic concentration. The errors in calculating osmotic-pressure and activity coefficients (given in Table IV) are not greater than 0·3% at 0·005 mm. pressure of mercury in a 0·2 M. solution.

TABLE IV.- OSMOTIC AND ACTIVITY COEFFICIENT DATA FOR AQUEOUS SOLUTIONS OF RUBIDIUM NITRATE FROM VAPOUR PRESSURE MEASUREMENTS

Solution Strength M.	Osmotic Coefficient ϕ	Activity Coefficient γ
0·1	0·903	0·727
0·5	0·811	0·532
1·0	0·745	0·427
1·5	0·698	0·364
2·0	0·656	0·318
2·5	0·620	0·283
3·0	0·588	0·255
3·5	0·562	0·234
4·0	0·539	0·215
4·5	0·517	0·199

At concentrations of aqueous rubidium nitrate solution greater than 2 M., the molecular volume is not a linear function at 18° and 25°C. but is parabolic.[21] Table V gives the relative viscosities and relative densities of aqueous solutions from 0·092 M. to 1·786 M. at 18° and 25·01°C. The viscosity–concentration curves at both temperatures are similar for potassium nitrate and caesium nitrate. The relation between relative viscosity and concentration for solutions below 0·2 N. is represented by the Jones–Dole[22] equation $\phi = 1 + A\sqrt{c} + Bc$ where ϕ = fluidity, and the constant B is negative for salts that increase the viscosity of water and positive for those that lower it. The stiffening effect of the interionic forces which determine the viscosity at high dilution tends to make the constant A negative.

TABLE V.- RELATIVE VISCOSITIES AND RELATIVE DENSITIES OF RUBIDIUM NITRATE SOLUTIONS

Temperature °C.	Concentration c mols./l.	Relative Viscosity ϕ	Relative Density d
18	0·09244	0·99251	1·00977
18	0·89168	0·94100	1·10114
18	1·78637	0·93388	1·22196
25·01	0·09244	0·99422	1·00966
25·01	0·89168	0·95877	1·10027
25·01	1·78637	0·96394	1·22028

Refs. p. 2255

At dilutions greater than 0·01 N. the effect of a strong electrolyte like rubidium nitrate is to make the viscosity of the solution greater than unity. The results[23] in Table VI confirm the ionic-atom theory of strong electrolytes.

TABLE VI.- RELATIVE VISCOSITIES AND RELATIVE DENSITIES OF DILUTE SOLUTIONS OF RUBIDIUM NITRATE

Temperature °C.	Concentration mole/l.	Relative Viscosity ϕ	Relative Density d
18	0·00199	1·00002	1·00021
18	0·01000	0·99931	1·00105
18	0·10000	0·99155	1·01044
35	0·00259	1·00015	1·00027
35	0·02204	0·99976	1·00226
35	0·10000	0·99704	1·01025
35	1·0000	0·98000	1·10100

Jaeger and Kapma[24] made some very accurate determinations of the electrical conductivities of molten salts over a wide range of temperatures, and reduced their results to a general expression for each of several salts of the alkali metals. For rubidium nitrate over a temperature range from 318·8°C. to 493°C.,

$$\mu_t = 33{\cdot}51 + 0{\cdot}145\ (t - 300)$$

This formula gives good agreement with the experimental results. The electrical conductivity of the binary melts of cadmium nitrate and rubidium nitrate[25] between 150°C. and 320°C. increases as the proportion of the cadmium salt decreases. But there is no irregularity at the composition corresponding to the compound $Cd(NO_3)_2,2RbNO_3$, neither was it noticed on the curves of temperature coefficient against composition. At 260°C. the conductivity was 0·206 for the equimolecular mixture. The dielectric constant of rubidium nitrate in aqueous solution of 0·0015 g.-equivalents per litre has been determined by means of high frequency measurements.[26] The constant decreases linearly when the concentration of the solute increases in water or water–glycerol mixtures. In an investigation[27] of the types of particles occurring in concentrated electrolytes van Ruyven has used vapour pressure data to study their degree of dissociation and the hydration. Raoult's law was employed together with Arrhenius' hypothesis in the treatment of these data by Tamman[28] and Remy.[29] No single electrolyte gave exclusively naked ions, and the degree of hydration increased with decreasing atomic volume for the alkali metal series Li^+, Na^+, K^+, Rb^+. Table VII gives a summary of results for the equilibrium constant K and the vapour pressure at 100°C. found for various concentrations of rubidium nitrate.

TABLE VII.- EQUILIBRIUM CONSTANTS AND VAPOUR PRESSURE OF VARIOUS CONCENTRATIONS OF RUBIDIUM NITRATE AT 100°C.

Normality N_w	Equilibrium Constant K	Vapour Pressure a_p
0·5	–	0·61
1	1·05	0·66
2	1·45	0·63
3	1·17	0·54
4	1·11	0·49
5	1·32	0·48

Refs. p. 2255

The heat of hydration $H^{\pm}$ (kg.-cal./mole), based on measurements of heats of solution (L) at infinite or very high dilution and the values of lattice energy (U), has been given by Mishchenko[30] as 143 for rubidium nitrate. The lattice energy value can be uncertain up to ±2% and this, on the average, will apply to his values for heat of hydration. His figures are more comprehensive than those of Bernal and Fowler and sometimes differ from them. The ionization equivalent constant (K_1) was found to be 1·47 for rubidium nitrate,[31] which is close to the values for all of the alkali metal nitrates. It had previously been reported as 2·11. Rubidium nitrate shows a weaker association capacity than does caesium nitrate. There is no hydration of rubidium and nitrate ions at 100°C. The association of nitrate ions with undissociated molecules, for example rubidium nitrate, can give rise to complex anions, such as $(RbN_2O_6)^-$. Under normal pressure the thermal dissociation[32] of rubidium nitrate takes place at 548·5°C. Binary mixtures of the alkali metal nitrates dissociate at temperatures between those for the single nitrates. The molar energy of interaction[33] of ions of the nitrate in concentrated aqueous solution is related to $\sqrt{C}$, where C is the volume concentration of the electrolyte in g.-mol./l. of solution. The deviation from this relation of strong electrolytes can be caused by the formation of liquid hydrates of ions of various stoicheiometric compounds that are able to dissociate in the solution. For aqueous solutions of rubidium nitrate between 0·5N. and 4·5N. the constants a and b are 0·151 and 1·017 respectively in the expression:

$$\omega = a + b\sqrt{C}$$

where ω is the molar energy of interaction of the ions.

APPLICATIONS AND BIOLOGICAL PROPERTIES

The luminescence of phosphors can be increased by the addition of several activators.[34] The mixture $14Sr(OH)_2$ (phosphor) + 4S + 6MgO + $0{\cdot}6Bi(NO_3)_3$ + $0{\cdot}3RbNO_3$ + $0{\cdot}6Na_2SO_4$ + $0{\cdot}6K_2SO_4$ + $2Li_2CO_3$ + 1·2 starch gives a blue-green phosphorescence. But the successive subtraction of the potassium sulphate, sodium sulphate, rubidium nitrate and lithium carbonate deminishes the luminescence progressively.

Although solutions of rubidium nitrate of more than 0·0005% concentration retard the growth of rye roots, Wolkenhauer[35] has found that 0·01% solution of the salt permitted growth equal to that of the control plants.

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SECTION LXXVI

RUBIDIUM PHOSPHATE

By N. M. HOPKIN

Physical properties

Rubidium phosphate exists in two crystallographic forms,[1] (I) monoclinic and (II) tetragonal. The monoclinic variety is obtained by the dilution of a saturated solution containing an excess of orthophosphoric acid, while neutral solutions inoculated with potassium or ammonium phosphate give the tetragonal form. Jaffe[2] prepared monoclinic crystals of the phosphate by rapidly cooling a concentrated solution. He obtained the tetragonal form by slowly cooling the saturated solution and also by evaporation from a saturated solution at room temperature. The tetragonal form is seignetto-electric in the direction of the *c* axis, obeying the Curie–Weiss law with its Curie point at 145·9 ± 0·3°K. Most authors[3] are in agreement about this value. This crystal behaves like those of the potassium dihydrogen phosphate and the potassium dihydrogen arsenate groups. These transition temperatures are associated with the orientation of the hydrogen bonds and are of the order–disorder type. No transition point has been found in rubidium dideuterium phosphate; this may be due to the formation of a lattice similar to that of the metastable rubidium phosphate.

Rubidium dihydrogen phosphate modifies the seignetto-electric properties[4] of potassium dihydrogen phosphate crystals by lowering the temperature of the Curie point and the maximum resonance temperature. Rubidium dideuterium phosphate also lowers the temperature coefficient of these piezo-crystals. The elasticity[6] of rubidium phosphate is similar in magnitude to that of potassium dihydrogen phosphate over the temperature range −50° to 30°C. Jona[6] confirmed this when determining the elastic constants for Rochelle salt, potassium di-deuterium phosphate and sodium chlorate by means of a method involving the differences of the diffraction of light on supersonic waves.

The electrical resistivity of piezo-crystals of the dihydrogen phosphate type is influenced by the presence of traces of impurities in the solutions from which they are grown. Barium and sulphate ions are particularly undesirable[7] because their ionic radii are similar to those of ammonium and phosphate ions respectively. They can therefore enter the crystal lattice with ease. A solution containing 0·0016% of $SO_4^=$ calculated on the ammonium dihydrogen phosphate can give crystals of an average resistivity of 25,000 megohms $cm.^{-1}$. The addition of small amounts of isomorphous rubidium phosphate of the order of 0·05% to 0·1% to the solution from which the piezo-crystals are grown will improve this figure to 37,000 megohms $cm.^{-1}$. At 9500 Mc. the complex dielectric constants of rubidium dihydrogen phosphate vary rapidly at 250°K., indicating transformations of the second order; these may be ferro-electric. This was first observed by Le Bot[8] *et al.* in 1953. This phosphate, which is isomorphous with its potassium analogue, has its maximum resonance frequency at −40°C.[9] Crystallographic data for a large number of Kurrol salts were determined by Corbridge[9] and for the corresponding compound of rubidium, $(RbPO_3)_n$ he gives: a 12·12, b 4·23, c 6·48 A.; β = 85°; 4 mols/unit cell; $d_{obs.}$ 3·29 g./c.c.; $d_{calc.}$ 3·32; space group = $P2_1/n$.

Bengtsson[10] prepared the monetite of barium and rubidium by mixing together the theoretical amounts of barium hydrogen phosphate and rubidium carbonate. The mixture was heated for three days. During the first day the temperature was slowly raised to 1000°C. and the mixture was ground at frequent intervals. The resulting hard product was slowly cooled. An X-ray study of the powder showed an orthorhombic diagram similar to that of rubidium sulphate. The lattice measurements were; a = 5·73, 5·97; b = 10·06, 10·43; c = 7·79, 7·81 A.; and V = 449 and 486 A.[3] The general shrinkage of the monetite lattice is due to the smaller radius of the barium ion compared with that of rubidium.

Chemical properties

The decomposition[11] of acid rubidium phosphate has been studied by means of temperature-time curves obtained when heat is applied at a constant rate. Breaks in such curves will show when endothermic reactions occur, such as the evolution of water or oxygen. The temperature of decomposition varies with pressure, being 310°C. at a pressure of 30 mm. of mercury and between 410 and 430°C. when the pressure is 710 mm. At still lower[12] pressures approaching vacuum conditions, the thermal decomposition of the phosphate is similar to that of potassium dihydrogen phosphate which occurs at about 250°C. The pyrophosphate loses half its water of crystallization at this temperature, but the remainder is eliminated more slowly, probably owing to the formation of a diacid tetraphosphate of rubidium.

The hydration of rubidium pyrophosphate in dilute solution is very slow. This was observed by Balareff[13] while investigating the structure of pyrophosphoric acid. He obtained a yellow precipitate with silver nitrate only after boiling a 1% solution of rubidium pyrophosphate for 15 hr.

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SECTION LXXVII

THE SPECTROSCOPY OF RUBIDIUM AND CERTAIN OF ITS COMPOUNDS

By R.F. BARROW and LADY ANNE THORNE

THE SPECTRUM OF ATOMIC RUBIDIUM

By A. THORNE

General Discussion and Excitation of the Spectrum

Introduction.

The spectrum of atomic rubidium has attracted much attention since the early days of spectroscopy, and indeed the study of the alkali-metal spectra played an important part in the development of modern spectroscopic theory. Brief historical accounts with references are given in most of the standard text-books on spectroscopy and in certain review articles.[1-3,17,18]

A description of the rubidium spectrum and its explanation in terms of modern theory is also to be found in standard text-books.[1-6] The neutral rubidium atom has the ground state electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 5s\ {}^2S_{1/2}$, with the $5s$ electron outside a krypton-like core of closed shells, giving rise to a doublet spectrum. The first doublet of the principal series lies in the near infra-red at 7800 A. and 7948 A. and the second in the violet at 4202 A. and 4216 A.; the rest of the principal series is in the ultra-violet. Most of the sharp and diffuse series lie in the visible, while the fundamental is in the infra-red. The most important energy levels and transitions of Rb I are shown diagrammatically by Grotrian.[7] Numerical values of experimentally determined energy levels of Rb I and II have been tabulated by Bacher and Goudsmit[8] and, more recently and more comprehensively, by the National Bureau of Standards for the spectra Rb I–III and IX–XIV.[9]

Measured wave-lengths and intensities of spectral lines were first arranged in series by Fowler[10] and Paschen-Götze[11] for the Rb I spectrum. Later tables compiled by Moore[12,13] give a few multiplets of astrophysical interest in the Rb I and II spectra, together with a finding list arranged by wave-length. The M.I.T. wave-length tables,[14] which list the arc and spark lines of all elements between 10,000 A. and 2000 A. in order of wave-length, include a list of the 'raies ultimes'; these are also given in the Vatican Observatory 'Atlas of Persistent Spectra'.[15] The use of certain rubidium lines as reference lines in the near infra-red has been discussed.[16]

In 1938 Shenstone[17] published a summary of spectroscopic work on the arc and spark spectra of all elements, incorporating tables showing how thoroughly each spectrum had been investigated. Meggers[18] brought the information up to date in 1946, and at the same time Hartree[19] presented in a similar way a summary of the calculations of wave functions and energy levels.

Astrophysics.

Rubidium has been identified in the sun by the presence of its resonance lines in the near infra-red part of the solar spectrum.[20,21]

Excitation of the Spectrum.

The spectrum of rubidium has been excited in flames, arcs, sparks and various forms of discharge. Reference is here made only to those papers in which the conditions or mechanism of excitation have been the main consideration. Accounts of wave-length and intensity measurements and of specialized light sources for particular investigations are given elsewhere; in particular, references to spark sources are given in the sub-section on the spectrum of ionized rubidium (see page 2264).

In flames several investigations have been made of the relation between the intensity of the spectral lines and the concentration of the rubidium salts. This relation has generally been found to follow a linear law at low concentrations and a square-root law at higher concentrations.[22-25,43] The process of excitation appears to be thermal.[25,43] Different methods of introducing the salt into the flame have been described,[22,25,29] and the effect on the intensity of the rubidium lines of adding other alkalies has been studied.[26-28]

In the electric furnace, lines have been observed in emission as well as absorption.[30] Chemiluminescence arising from the interaction of rubidium vapour with the halogens has been investigated.[31]

Lines of both the Rb I and Rb II spectra have been excited by collisions with hydrogen and helium atoms.[32]

In rubidium arcs studies have been made of the effect of the voltage on the excitation of the spectrum[35] and of the temperature distribution and electron density within the arc.[33,34] An interrupted arc has been found to give many lines of Rb II.[36] Convenient lamps for production of the Rb I spectrum have been developed.[37,44]

In glow discharges passed through mercury vapour mixed with the vapour of rubidium or of the other alkali metals, relative intensities have been measured,[38,39] and the spectrum of the positive column of a discharge containing rubidium vapour has been studied.[40] Electrodeless discharges are found to excite both the arc and the spark spectra of rubidium.[41,42]

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The Spectrum of Neutral Rubidium

The ground state of the neutral rubidium atom is $5s\ ^2S_{1/2}$, with a krypton-like core of closed shells. The ionization potential of 4·176 volts corresponds to term values for the ground state of 33,691·02 ± 0·03 cm.$^{-1}$ and 33,691·10 ± 0·03 cm.$^{-1}$ for ^{85}Rb and ^{87}Rb, respectively.[1]

Fowler's 1922 tables[3] list the first 30 doublets of the principal series, 6 of them resolved, 8 members of each of the sharp and diffuse series, and a few of the fundamental. Some higher members of the principal series are included in Moore's ultra-violet multiplet tables.[2] The information summarized by Fowler was subsequently extended by measurements on the principal series in absorption[4,5] and on infra-red lines.[6] Ramb measured several members of the sharp, diffuse and fundamental series interferometrically,[9] and a few strong lines were also measured interferometrically by others.[7,8] More recently Kratz[10] observed the principal series in absorption as far as $n = 77$, the doublets being resolved up to $n = 26$. These results, together with some on forbidden lines,[21-23] are all incorporated in the National Bureau of Standards 'Atomic Energy Levels', 1952,[1] which tabulates the experimentally determined term values for excited states of the $5s$ electron from $6s$ to $12s$ and $32s$ to $53s$, from $5p$ to $77p$, from $4d$ to $54d$, from $4f$ to $8f$ and $29f$ to $47f$, $5g$, $6g$ and $6h$.

Apart from the first 22 ^2P intervals resolved by Kratz,[10] some ^2D intervals were measured by Ramb[9] and others[11,12,22] and some ^2F intervals by Meissner and Masaki.[13] The first ^2D and the ^2F terms are inverted, an effect generally ascribed to perturbations by excited states of the core electrons.[58-62] Table I gives the ^2D and ^2F intervals as far as they have been measured and the first few ^2P intervals. As far as they have been resolved, the ^2P intervals obey closely the law $\Delta\nu \propto 1/n^{*3}$ where n^* is the effective principal quantum number.[10]

Beutler has found in absorption 40 lines of the so-called Rb I^b spectrum,[14,15] arising from the excitation of an electron from an inner shell, in this case the $4p^6$ shell. Most of these lines are classified as $4p^6\ 5s$ - $4p^5\ 5s\ ns$ and $4p^6\ 5s$ – $4p^5\ 5s\ nd$ transitions, having as series limits the excited $4p^5\ 5s$ ^3P and ^1P terms of Rb II. The Rb I levels derived from these transitions are

TABLE I. - DOUBLET INTERVALS IN THE SPECTRUM OF Rb I

n	4	5	6	7	8	9	10	11	12	13
$\Delta(n^2P)$(cm.$^{-1}$)		237·60	77·50	35·09	18·86	11·28	7·31	4·97	3·54	2·60
$\Delta(n^2D)$(cm.$^{-1}$)	−0·44	2·96	2·26	1·51	1·01	0·70	0·48	0·30	0·25	0·20
$\Delta(n^2F)$(cm.$^{-1}$)		−0·01	−0·01	−0·01						

included in 'Atomic Energy Levels'.[1]

Forbidden lines of the $5s - nd$ series have long been known in both emission and absorption.[16,17] Measurements of their intensity are in agreement with the transition probabilities to be expected for quadrupole radiation.[18-20] This series was recently extended by the absorption measurements of Kratz and Mack as far as $5s - 54d$.[22] In addition, they found a long $5s - ns$ series running from $n = 32$ to $n = 52$ and another long series designated as $5s - nq$, where nq represents higher members of the f, g, or h series.[21-23] Lines of the forbidden $p - p$ series have been found in emission, and some intensity measurements made on them.[24,25] The absorption of both the $s - d$ and $s - s$ series in external electric fields is referred to under the Stark effect (see page 2266).

The continuous emission (recombination) spectrum of rubidium has been studied in different sources.[25-27] The continuous absorption (photo-ionization) spectrum has also been investigated,[28,29] and Ditchburn *et al.*[30] have compared the variation of atomic absorption coefficient with frequency in all the alkali metal vapours: the minimum just below the series limit, which is characteristic of the other alkalies, has not been definitely established for rubidium. Quantum-mechanical calculations of continuous absorption coefficients as a function of frequency have been compared with the experimental results.[63,64]

The measurement of transition probabilities in atomic lines has been discussed fully by Mitchell and Zemansky,[47] and more recent work is referred to in Unsöld's book.[48] For rubidium, the transition probabilities of a few members of the principal[31] and of the sharp and diffuse series[32] have been found from the absolute intensities of emission, and the method of anomalous dispersion has been applied to the principal series.[33] A recent determination by the null method of magneto-rotation[34,35] in the resonance doublet gives lifetimes of $2{\cdot}85$ and $2{\cdot}78 \times 10^{-8}$ sec. for the $^2P_{1/2}$ and $^3P_{3/2}$ states, respectively, corresponding to f-values of 0·335 and 0·661. Measured intensities have been discussed with reference to thermodynamical equilibrium for the sharp and diffuse series.[36]

Considerable attention has been devoted to the doublet intensity ratio in the principal series. Early measurements gave contradictory results,[37-39,44] but it was later established that, at least for the higher series members, the ratio is greater than the theoretical value of 2:1. Most results indicate a ratio of about 3:1 for the second member and still higher ratios for the higher members.[31,40-43] Fermi has suggested a theoretical explanation for the departure from the 2:1 rule.[45,46]

Little theoretical work has been done on the spectrum of rubidium. Although, as stated in the Introduction, the spectra of this and the other alkali metals were much studied in connection with the development of the theory of atomic spectra, calculations of energy levels for atoms as heavy as rubidium have seldom been carried beyond the semi-empirical stage.[49-52] The application of quantum mechanics to the determination of atomic energy levels and eigenfunctions has been fully set out by Condon and Shortley.[53] Hartree in 1946 summarized the calculations carried out up to that date on the spectra of all light and a few heavy atoms for states of ionization up to the fourth.[54] For rubidium, the only published values of wave functions appear to be self-consistent field functions without exchange for the ground state of Rb^+.[55-57]

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The Spectrum of Ionized Rubidium

Singly Ionized.

Lines of the Rb II spectrum have been identified in several different kinds of source, for example in certain combustion and collision processes[3,4] and in interrupted arcs,[9] as well as in the electrodeless discharges,[7,8,16] hollow-cathode discharges,[14,15] and various forms of spark used in systematic investigation of the spectrum. The conditions of excitation in sparks have been studied.[5,6]

The lines first measured[7,8] were classified by comparison with iso-electronic spectra.[10-12] The results of these measurements were added by Laporte, Miller and Sawyer to their own results to give a total of 33 levels derived from 107 classified lines.[14,15] This work forms the basis of the Rb II energy levels listed in the National Bureau of Standards 'Atomic Energy Levels',[1] although a few additional measurements have been reported.[13,16] Moore's ultra-violet multiplet tables[2] give the wave-lengths of only a few Rb II multiplets.

Rb II in the ground state has the krypton-like electron configuration $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^2$ $4p^6$ $^1S_0$, with an ionization potential of 27·5 V., corresponding to a series limit (for the $^2P_{3/2}$ ground term of Rb III) of 221,852 cm.$^{-1}$; the series limit for the $^2P_{1/2}$ term is 229,232 cm.$^{-1}$ 'Atomic Energy Levels'[1] lists terms built on both the $4p^5$ $^2P_{3/2}$ and the $4p^5$ $^2P_{1/2}$ terms of the ion, with configurations $4p^5$ 5,6s; $4p^5$ $5p$; and $4p^5$ 4,5d. Later measurements have modified the fine structure of certain of these terms.[17]

Doubly Ionized.

Rb III has a bromine-like spectrum, with the ground-state configuration $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^2$ $4p^5$ $^2P_{3/2}$. Thirty lines of Rb III have been classified by Tomboulian and a few additional lines reported by others.[16] 'Atomic Energy Levels'[1] lists the eleven terms derived from Tomboulian's measurements, arising from the configurations $4s^2$ $4p^5$, $4s^2$ $4p^4$ $4d$, and $4s^2$ $4p^4$ $5s$. The ionization potential is 40 V., corresponding to a series limit of 320,000 cm.$^{-1}$

More Highly Ionized.

The spectra of Rb IV and higher ions have not been analysed. However, Mack[19] has identified the resonance doublet of Rb IX, and Edlén[20] has observed a few lines in each of the spectra Rb X – Rb XIV. Table II indicates the extent to which each of these spectra is known, as reported in 'Atomic Energy Levels'.[1]

TABLE II. - DATA ON THE SPECTRA Rb IX TO Rb XIV.

Spectrum	Iso-electronic with	Ionization Potential (volts)	Series Limit (cm.$^{-1}$)	Ground State $1s$ $2s$ $2p$ $3s$ $3p$ +	Configs. of which terms identified
IX	Cu I			$3d^{10}$ $4s$ $^2S_{1/2}$	$3p^6$ $3d^{10}$ $4p$
X	Ni I	277	2,235,100	$3d^{10}$ $^1S_0$	$3p^6$ $3d^9$ 4,5p; 4–6f
XI	Co I			$3d^9$ $^2D_{5/2}$	$3p^5$ $3d^{10}$
XII	Fe I			$3d^8$ $^3F_4$	$3p^6$ $3d^7$ $4p$
XIII	Mn I			$3d^7$ $^4F_{9/2}$	$3p^6$ $3d^6$ $4p$
XIV	Cr I			$3d^6$ $^5D_4$	$3p^6$ $3d^5$ $4p$

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Zeeman, Stark and Pressure Effects

Zeeman Effect.

The Zeeman effect in the alkali metal doublets is described in standard text-books on spectroscopy, for example those already cited (see page 2260). Rather fuller accounts have been given by Back and Landé.[1,2] As the historical resumés in these books indicate, the 'anomalous' Zeeman pattern of the resonance lines of the alkali metals played an important part in the development of spectroscopic theory.

The Landé *g*-factor for the $^2S_{1/2}$ ground state of rubidium is 2, and for the $^2P_{1/2}$, $^2P_{3/2}$ levels it is 2/3 and 4/3, respectively. Thus, in terms of the classical Lorentz splitting $\Delta\nu_L$, the $^2S_{1/2}$–$^2P_{1/2}$ line has two σ components at $\pm\frac{4}{3}\Delta\nu_L$ and two π components at $\pm\frac{2}{3}\Delta\nu_L$, while the $^2S_{1/2}$–$^2P_{3/2}$ line has four σ components at $\pm\frac{2}{3}\Delta\nu_L$, $\pm\frac{5}{3}\Delta\nu_L$ and two π components at $\pm\frac{1}{3}\Delta\nu_L$. The Paschen-Back effect sets in at magnetic field strengths sufficient to break down the spin-orbit coupling; as this condition is approached, the components of the two resonance lines merge to form a Lorentz triplet with unshifted π component and σ components at $\pm\Delta\nu_L$. The Zeeman effect in the alkali metals has been treated theoretically on the basis of Dirac's theory.[4]

The Zeeman effect in the ground state of rubidium has received much attention in atomic beam magnetic resonance experiments (see also page 2268), in the course of which extremely accurate measurements of the Zeeman splitting have been made.[5] The $g(^2S_{1/2})$ value of rubidium is found to differ from that of the three lighter alkali metals by $5:10^5$. Reasons for this discrepancy have been suggested.[6]

The magnetic double refraction of rubidium vapour has been measured and compared with the calculated effect.[7] The appearance of 'forbidden' components in the Zeeman pattern of the resonance lines has been described[8,9,21,47] and calculations made of their intensity.[10,47] Pressure broadening of the Zeeman components has also been investigated.[21]

The simple Zeeman pattern in any field is symmetrical about the field-free line. However, at high fields and for the higher members of a series, the pattern as a whole may be asymmetrically shifted by the so-called quadratic

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Zeeman effect. Theoretically, the centre of gravity of the σ components should be shifted twice as far as that of the π components, the shift being proportional to H^2 and to $(n^*)^4$, where n^* is the effective quantum number.[11] Experimental results for rubidium are in reasonably good agreement with the theory.[12]

Stark Effect.

The Stark effect is rather briefly discussed in most text-books. A fuller account has been given by Minkowski.[3] The Stark pattern of a line is considerably more complicated than its Zeeman pattern. In the alkali metals the first-order effect is a quadratic one: an asymmetric splitting proportional to the square of the field strength, which, when unresolved, appears as a simultaneous broadening and shift of the line. The theory of the effect in the alkali metals has been discussed in several papers.[13-15]

Experimental investigations appear to have been confined to absorption measurements on the principal series.[16-20] These show the quadratic effect,[17-19] but in higher members of the series the linear effect appears.[20] The electric field also has the effect of bringing up lines of the forbidden $s - s$ and $s - d$ series, and its effect on the intensities and positions of these lines has been discussed.[18-20]

Pressure Effects.

General accounts of the effects of pressure on spectral lines may be found in text-books[22,23] and in the review articles written in 1936 by Margenau and Watson[24] and in 1957 by Ch'en and Takeo;[25] both the latter contain references to experimental work on alkali-metal spectra, on which some of the most extensive research has been done, and accounts of the theories of pressure effects, including the Stark effect due to inter-atomic electric fields. More detailed theoretical papers have been published on both foreign gas broadening[26-29]and 'resonance' (self-pressure) broadening.[30,31]

Several measurements have been made of the broadening and shifts of the first two doublets of the rubidium principal series in absorption in the presence of different foreign gases at pressures of up to several hundred atmospheres.[21,32-36] The direction of the shift depends on the gas used, and the two members of the doublet are affected differently.[33-35] A number of measurements have also been made on higher members of the principal series. The shift is proportional to the relative density of the foreign gas and appears to approach a constant value at the series limit.[37-40]

The appearance of bands near the absorption lines of rubidium in the presence of foreign gases has been attributed to the formation of loosely bound polarization molecules.[33,41-43]

The broadening of the resonance lines with increasing pressure of rubidium vapour has been measured and compared with the line contours to be expected from the dispersion formula[44,46] and, at high vapour pressures, the formation of quasi-molecules.[45,46]

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Hyperfine Structure and Nuclear Moments

Before the development of magnetic resonance techniques, nuclear moments were determined primarily by optical investigation of the hyperfine structure (hereafter referred to as hfs). Kopfermann[1] has given a very full account of the theoretical background and of the methods of both optical and radiofrequency spectroscopy, and Ramsey[2] has summarized the application of these methods to the determination of nuclear moments, giving tables of results up to 1952 and many references. Nuclear effects in atomic spectra[33] and the rôle of nuclear moments in the shell model of the nucleus[35] have recently been reviewed.

The data for the rubidium isotopes are summarized in Table III, in which references are given only for the results published since 1952 and therefore not included by Ramsey.[2]

In this Table I is the nuclear spin, μ the nuclear magnetic moment (in nuclear magnetons) and Q the nuclear electric quadrupole moment. The columns headed $\Delta\nu(5^2S_{1/2})$ refer to the splitting between the two hyperfine levels of the $5s\ ^2S_{1/2}$ ground state; this has been measured much more accurately by radiofrequency methods than is possible optically (as has the magnetic moment),[34]

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TABLE III. - NUCLEAR MOMENTS OF THE RUBIDIUM ISOTOPES

Isotope	I	μ (n.m.)	Q ($\times 10^{-24}$ cm.^{2})	$\Delta\nu(5^2S_{1/2})$	
				mc/s	cm.$^{-1}$
^{81}Rb	$\frac{3}{2}$[19]	+2·00[19,20] ±0·06		5000[19,20] ± 125	0·167
^{82}Rb	5[19]				
^{83}Rb	$\frac{5}{2}$[19]				
^{84}Rb	2[19]				
^{85}Rb	$\frac{5}{2}$	+1·3532 ±0·0004	0·29[32] ±0·02 or 0·27[30] ±0·02	3035·7 ± 0·2	0·1013
^{86}Rb	2[17,18]	−1·69[18] ±0·01		3960[18] ± 20	0·132
^{87}Rb	$\frac{3}{2}$	+2·7501 ±0·0005	0·14[11,32] ±0·01 or 0·13[30] ±0·01	6834·1 ± 1·0	0·2280

but the first few figures of the value have here been converted for convenience to cm.$^{-1}$

First attempts to determine the spins of the two naturally occurring isotopes, ^{85}Rb and ^{87}Rb, from intensity measurements on the optical hfs gave incorrect results,[3-5] but Kopfermann and others later succeeded in determining the spins from the spectrum of Rb II[6] and in resolving the hfs of the resonance lines of Rb I.[6,8,9] The hfs of the ^{2}P levels was unresolved but calculable from the pattern. The values found[8,9] for the two isotopes are given in Table IV, in units of cm.$^{-1}$

TABLE IV. - HFS INTERVALS IN THE SPECTRA OF ^{85}Rb AND ^{87}Rb

	$\Delta\nu(5^2S_{1/2})$	$\Delta\nu(5^2P_{1/2})$	$\Delta\nu(5^2P_{3/2})$
^{85}Rb	0·228	0·017	0·009
^{87}Rb	0·101	0·027	0·014

The results of hfs measurements on the alkali metals in the 1930's have been summarized.[10] In rubidium the isotope shift[1,33] has been found to be zero for the ground state of the isotopes ^{85}Rb and ^{87}Rb.[7] A theoretical estimate of the shifts to be expected in the rubidium spectrum has recently been made.[37]

From a very recent investigation of certain terms of the Rb II spectrum[11] the electric quadrupole moment of the ^{87}Rb nucleus has been determined as $0{\cdot}14 \pm 0{\cdot}06 \times 10^{-24}$ cm.^{2}

The most accurate measurements of nuclear moments and of the hfs and Zeeman levels of the ground state have been made by radiofrequency methods, mainly in atomic and molecular beams.[1,2,34] The atomic beam method of zero moments was early applied to find the spins and hyperfine structures of ^{85}Rb and ^{87}Rb.[12] Later Rabi's magnetic resonance technique was used in atomic beams of rubidium to measure accurately the ground-state hfs and Zeeman effect of both these isotopes[13,14] and in molecular beams to measure directly their magnetic moments.[15,16] From magnetic resonance experiments on atomic beams of the radioactive isotopes of rubidium, the spin, ground-state hfs and magnetic moment of ^{86}Rb have been determined,[17,18] and the spins of the isotopes ^{81,82,83,84}Rb.[19] Values for the hfs and magnetic moment of ^{81}Rb have also been found by the zero-moment method.[20]

By nuclear magnetic resonance methods several very precise determinations have been made of the ratios of the nuclear magnetic moments of ^{85}Rb and ^{87}Rb to that of the proton and to each other.[21-26] The latter ratio is of particular interest in connection with the so-called hfs anomaly, or Bohr-Weisskopf effect, the result of the distribution of the magnetic moment over a finite nuclear volume.[27-29]

Recently Rabi *et al.* have succeeded in performing atomic beam magnetic resonance experiments with alkali-metal atoms in excited ^2P states, and from transitions between hyperfine levels of the $5^2P_{3/2}$ and $5^2P_{1/2}$ states of both ^{85}Rb and ^{87}Rb they have found the magnetic hfs constants of these states and the electric quadrupole moments of both nuclei[30] ($0{\cdot}27 \pm 0{\cdot}02$ and $0{\cdot}13 \pm 0{\cdot}01 \times 10^{-24}$ cm.^{2}, respectively). Perturbations apparent from these measurements have been discussed.[31] In addition, the hfs of the $6^2P_{3/2}$ state has been investigated by the very recent technique of magnetic double resonance, whereby radiofrequency transitions between hyperfine levels are detected optically. The values of Q found in this way are in good agreement with the atomic beam values.[32] The ratio of $Q_{85}:Q_{87}$ is confirmed by the value of $2{\cdot}0669 \pm 0{\cdot}0005$ found for it in magnetic resonance measurements on a beam of RbCl molecules.

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X-Ray Spectrum

Early work on the X-ray spectrum of rubidium was principally concerned with measurements of the wave-lengths and intensities of the K- and L-series lines and absorption edges.[1-3] Tables of atomic energy levels have recently

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been compiled from X-ray frequencies for rubidium and other light and medium elements.[7,16]

Certain faint lines in the X-ray spectrum of rubidium have been ascribed to quadrupole transitions.[4] Others, appearing as satellites of K- and L-emission lines, are believed to originate in atoms in which a second electron has been knocked out of an inner shell.[5,6]

With the higher-resolution methods developed since the early years of X-ray spectroscopy, it has been shown that the absorption edges of atoms in the solid state have a fine structure and that, owing to the influence of free electrons and neighbouring atoms, many of the emission 'lines' are in fact bands of varying width. The structure of the K-edge of rubidium in the metal and various crystals has been examined[8-10] and the widths of emission lines measured.[11,15] The results have been interpreted in terms of the electronic energy bands in the crystal lattice and the free electron conduction bands.[9,10]

General accounts and reviews discuss the X-ray spectrum of rubidium, with particular emphasis on the importance of X-ray spectroscopy in solid state physics.[12-14]

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THE MOLECULAR SPECTRA OF RUBIDIUM AND CERTAIN OF ITS COMPOUNDS

By R. F. BARROW

The Rb_2 Molecule

The spectrum of the Rb_2 molecule may be readily observed, for example in fluorescence[1] or absorption.[1,2] The magnetic rotation spectrum has also been observed.[6] Early vibrational analyses[3] were based on inadequate data, and no analysis has yet been given of the infrared bands[4,5] at 8400 to 9050A. Constants[6,7] for the Rb_2 molecule are given below.

State	T_e	ω_e	$x_e\omega_e$	$y_e\omega_e$	D_0kg.-cal.
D	22777·5	40·42	0·0745	-0·00144	3·9
C	20835·1	36·46	0·124	-	7·1
$B^1\Pi_u$	14662·6	48·05	0·191	-	8·5
A	~11500	-	-	-	-
$X^1\Sigma_g^+$	0	57·28	0·096	-0·00083	11·3±0·5

Bands arising from polarization molecules, Rb-Rb, or Rb-foreign gas have also been observed.[8-10]

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The RbCs Molecule

The analysis of one system of bands observed in absorption and first attributed[1] to Cs_2 has been given.[2] The constants are as follows:-

State	T_e	ω_e
A	13747·2	38·46
$X^1\Sigma^+$	0	49·41

A diffuse band at 5640A. has also been attributed to this molecule.[3]

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Rubidium Hydride

A discharge through rubidium vapour in presence of hydrogen gives rise to a many-lined spectrum in the region 4600 to 6600A. which is assigned to the molecule RbH. Constants[1] are as follows:-

State	T_e	ω_e	$x_e\omega_e$	$y_e\omega_e$	D_0, kg.-cal.
$A^1\Sigma^+$	18906·4	244·6	-4·1	-0·169	-
$X^1\Sigma^+$	0	936·77	14·15	+0·075	39±5

State	B_e	α_e	r_e, A.
$A^1\Sigma^+$	1·231	-0·023	3·708
$X^1\Sigma^+$	3·020	0·072	2·367

The excited state $A^1\Sigma^+$ shows anomalies similar to those observed for the other alkali hydrides[2] (see also LiH, p. 280). A theoretical treatment of the intensity distribution in this system has been given.[3]

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Rubidium Halides

The spectra of the rubidium halides in absorption in the vapour state have been investigated as follows:-
Microwave region: rubidium bromide[1] and iodide.[1]
Infra-red (vibration-rotation) region: rubidium chloride.[2]
Electronic spectra: rubidium fluoride,[6] chloride,[3,4,6] bromide,[3,6] and iodide.[5,6]

Rubidium fluoride[7], and rubidium chloride[8] have also been studied by the technique of molecular beam electric resonance. In the former work, the transitions J = 1 to J = 2 were observed, but in the latter, precise molecular constants were obtained from observations on the transitions J = 0 → J = 1. Radio-frequency spectra of rubidium fluoride and chloride have also been studied by the zero-field molecular-beam magnetic resonance method.[9-13]

Values of the molecular constants of these molecules are collected in Table V, together with the thermochemical information required for the determination of their energies of dissociation (see also Li, p. 283).

TABLE V. SPECTROSCOPIC CONSTANTS FOR THE GASEOUS RUBIDIUM HALIDES

Molecule	B_e	α_e	r_e, A.	ω_e, cm.$^{-1}$	μ, D.
RbF	-	-	[2·246]	(365)(4)	-
RbCl	2627·40(2)	13·601(2)	2·7868	228	-
RbBr	1424·84(3)	5·578(3)	2·9448	[166]	-
RbI	984·32	3·281	3·1769	[128]	-

Notes: (1) The values of B_e, α_e and r_e are taken from reference 1. The values of B_e and α_e are in Mc./sec.
(2) Constants for $^{85}Rb^{35}Cl$.
(3) Constants for $^{85}Rb^{79}Br$.
(4) ω_e (RbF) = 390 cm.$^{-1}$ from ultra-violet spectrum,[6] 340±70 cm.$^{-1}$ from mol-

continued on following page

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ecular-beam electric resonance.[7] Other values of ω_e are from reference 2: values in square brackets are estimated values.

TABLE V (continued)

Dissociation Energies, D_{298}, kg.-cal.mole^{-1}	RbF	RbCl	RbBr	RbI
$-Q_f(MX)$	131·28[a]	102·91[a]	93·03[a]	78·5[a]
$-\Delta_s H(MX)$	-54·9[b]	-50·4[d]	-49·3[d]	-46·7[d]
$\Delta_s H(M)$	$20{\cdot}50_5$[c]	$25{\cdot}50_5$[c]	$25{\cdot}50_5$[c]	$25{\cdot}50_5$[c]
$Q_f(X)$	18·86[d]	29·01[a]	26·71[a]	25·48[a]
D_{298}	115·75	107·0	$95{\cdot}9_5$	82·8

a reference 10
b reference 11
c reference 12
d recalculated from reference 14

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COMPOUNDS OF RUBIDIUM: SOLID STATE

Rubidium Hydride

The ultra-violet absorption of thin layers of rubidium hydride deposited on quartz has been examined.[1] Maxima occur at 2680 and 2020A.

Reference

1 Rauch, W., *Z. Phys.*, 1939,**111**,650-6. (*33*,6155)

Rubidium Oxide, Rb_2O

Maxima[1] in the ultra-violet absorption spectra of thin films of rubidium oxide deposited on quartz lie at 3470, 2960, 2540 and 1920A.

Reference

1 Rauch, W., *Z. Phys.*, 1940,**116**,652-6. (*35*,4682)

Rubidium Halides

In order to avoid repetition, certain properties of the crystalline alkali metal halides are only discussed in detail under one appropiate alkali metal, as follows: ultraviolet absorption spectra, page 285; Raman spectra, page 1380; colour centres, page 2012; luminescence: phosphors, page 2018.

The absorption spectra have been studied both in the infra-red and ultra-violet regions. In the infra-red, maxima have been observed[1] as follows:-

RbCl: 84·8μ. RbBr: 114·0μ. RbI: 129·5μ.

In the ultra-violet region, the maxima[2-4] lie at the following wave-lengths:-

RbF:	1320	1150A.				
RbCl:	1660	1380A.				
RbBr:	1910	1780	1550	1460	1230A.	
RbI:	2230	1870	1790	1560	1340	1200A.

The variation with temperature of the position of the longest-wave-length band of rubidium bromide[5] has also been studied (see also page 285).

The infrared absorption and reflexion spectra of rubidium bifluoride has been examined[6] in connexion with the structure of the bifluoride ion.

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Rubidium Nitrate

The ultra-violet reflexion spectrum of rubidium nitrate has been studied.[1]

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SECTION LXXVIII

THE ANALYTICAL DETERMINATION OF RUBIDIUM

By H. V. THOMPSON

DETECTION

The additions to the analytical reactions of rubidium subsequent to those previously given (Mellor,II,472-4), have been relatively limited[1,2] and there is a paucity of specific tests for the element, though in certain cases it can be detected microchemically in the presence of cæsium.

With a mixed solution of gold and silver, rubidium chloride forms blood red prisms and tables whereas small non-transparent cubes and stars are given by the corresponding cæsium compound.[3,4]

Rubidium salts in concentrated hydriodic acid, when treated with a solution of gold and silver iodides in the same acid, yield black hexagonal crystals of an aurous auric rubidium silver iodide. Cæsium salts react similarly, but the crystals tend to collect into stellate aggregates.[5] The triple chlorides of rubidium and caesium with gold and silver both form reddish crystals.[5a,10a] On adding a drop of a solution of auric and palladous chlorides to a drop of the test solution, a black compound of the type $M_2AuPdCl_7$ is precipitated if either rubidium or cæsium is present.[6-8,10a] However, the prior removal of caesium by precipitation as its double iodide with bismuth is said to render the test for rubidium unambiguous.[8] When drops of concentrated solutions of sodium bromide and rhodium chloride are added to a drop of a mixed solution of rubidium and caesium salts, crystals characteristic of both elements are formed.[9] Potassium, rubidium and cæsium can be separated by paper chromatography and detected by developing the chromatogram with sodium lead cobaltinitrite.[9a] As a result of an examination of the sensitiveness of various reagents for the detection of rubidium and cæsium, Moser and Ritschel conclude that the test with silicomolybdic acid is the most reliable in the presence of potassium, but in its absence the phosphotungstic acid test is the most delicate, followed by that with sodium cobaltinitrite.[10] According to Geilmann and Gebauhr few of the wet tests for potassium, rubidium and cæsium are entirely satisfactory.[10a]

Rubidium in a concentration of not less than 0·3% can be detected in the presence of 230 times its weight of cæsium by the formation of yellow needles when a neutral solution is treated with a solution of Naphthol Yellow S in pure formic acid.[11]

When present as traces rubidium and cæsium are detected spectroscopically,[12-19] but even so it may be necessary to effect an initial concentration of the two elements by applying a gravimetric separation from the other alkali metals (see page 2276) and examining spectroscopically the solid from the residual solution of the mixed salts of rubidium and cæsium.

DETERMINATION BY CHEMICAL METHODS

Gravimetric Methods.

The first step in the determination of rubidium or cæsium is the preparation by standard methods of a solution of the alkali metal chlorides free from all other constituents. From this point various routes can be taken to obtain a solution containing only rubidium and cæsium with, in certain cases, a small amount of sodium. In one process, potassium, rubidium and cæsium are separated as their chloroplatinates or perchlorates from the remaining alkali metals and subsequently converted into chlorides. Rubidium and cæsium are then separated from potassium by precipitation as 9-phosphomolybdates and, after removal of molybdenum as sulphide, the two metals are reconverted into chlorides through their chloroplatinates.[20]

In the sodium bismuthinitrite method,[21,22] the mixed alkali chlorides are converted into nitrates and rubidium and cæsium are precipitated as triple nitrites,[23] $X_2NaBi(NO_2)_6$, by adding a solution of bismuth nitrate in an excess of sodium nitrite. From the hydrochloric acid solution of the precipitate the bismuth is removed as sulphide, giving a solution containing only rubidium and cæsium together with a little sodium.

Other methods rely on the much higher solubility of rubidium and cæsium chlorides in mixtures of hydrochloric acid and ethyl alcohol to effect the separation of these two metals from potassium and sodium, if present,[24-28] but this procedure has had some adverse comment.[29-31]

Separation of Rubidium and Cæsium.

Owing to their close chemical similarity, it is doubtful whether any reagent effects a truly quantitative separation of these two elements, and in all methods the limiting factor is the difference in solubility of a given pair of salts. In the silicotungstate process[20] the rubidium and cæsium in the mixed solution are converted, if necessary, into chlorides and the cæsium is precipitated as silicotungstate. The rubidium is then directly determined in the filtrate as chloroplatinate. If, however, rubidium is present to the extent of 0·4% or more, it will be precipitated by an excess of the reagent.[32]

Godeffroy's test[33] has been adapted for quantitative work by precipitating the cæsium in the presence of ferric chloride as a complex chloride of cæsium and antimony, $Cs_3Sb_2Cl_9$, with a solution of antimony trichloride in glacial acetic acid, the ferric chloride being added to minimize the co-precipitation of rubidium.[24,25] After removing antimony and iron from the filtrate, the rubidium can be determined either as perchlorate or chloroplatinate. Moser and Ritschel were unable to get consistent results by this method and concluded that the separation was unsatisfactory.[29]

The difference in solubility of rubidium and cæsium sulphates in aqueous alcohol forms the basis of Wells and Stevens' method of separation in which the mixture of dry chlorides is treated with an alcoholic solution of ammonium sulphate, when sparingly soluble rubidium sulphate is formed.[26]

As the solubility products of the tetraphenyl boron complexes of rubidium and cæsium are approximately one tenth that of potassium,[34] this method (see page 2027) is applicable to rubidium or cæsium or to both elements in admixture after separation from potassium.[35] A volumetric method has been based on the decomposition of rubidium tri-iodide by carbon tetrachloride into the normal iodide and iodine, whereas the corresponding caesium salt is stable.[35a]

DETERMINATION BY PHYSICAL METHODS

In the normal course of analytical work, cæsium and rubidium are present only in minor or trace amounts; consequently considerable emphasis is placed on spectrographic analysis,[36-53,5a] not merely on account of speed in operation, but as giving in many cases more reliable results than purely chemical methods by which, as has been pointed out, a quantitative separation of the two elements is difficult to achieve. Rubidium has been determined by flame photometry[54,55] and, like potassium, by β-ray emission.[56]

Rubidium can be determined colorimetrically,[57] and all types of quantita-

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tive methods for rubidium and caesium have been reviewed, either separately or in conjunction with those for the other alkali metals, in a number of papers.[1,20,58-61]

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SECTION LXXIX

BIOLOGICAL PROPERTIES OF RUBIDIUM

By F. CALL

Rubidium is widely, though not abundantly, distributed in water and soil from which it is extracted and concentrated by living organisms. Thus, the average percentage of rubidium in sea water[1] is 2×10^{-5} and in marine organisms 3.4×10^{-4}; in rivers 1.6×10^{-7} and in fresh water organisms 2.9×10^{-4}; in soils 6×10^{-3} and in grasses 6.4×10^{-4}. In general rubidium can replace potassium to a large degree in its metabolic role in living organisms and the toxicity of rubidium appears to depend on its interference with potassium.[2,3]

Micro-organisms

Rubidium is the only element that can partially replace potassium in a number of yeasts, mycobacteria and aerobic spore-forming organisms.[4-7] The growth of yeast[8] and of *Aspergillus niger*,[9] as well as the fermentation of glucose by yeast[10] are all stimulated by rubidium salts. Rubidium can also act as a substitute for potassium in overcoming the inhibition by sodium or caesium ions of the glycolysis of *Lactobacillus arabinosus*.[11] The radioactive isotope ^{86}Rb has been used to study the uptake of rubidium by bacteria[12] and the element has been shown to enter the cells of *Aerobacter aerogenes* by the process of active transport and in addition to protect this organism from the effects of adverse pH.[13] Rubidium salts may also produce morphological changes in certain bacteria, e.g. the proliferation of filamentous forms.[14,15] Solutions of rubidium chloride at concentrations of 0.5–5.0 g. per l. cause fungistasis of *Torulopsis corallina*,[16] but injection of rubidium sulphate into mice and guinea pigs has no therapeutic action against the organism causing typhus.[17]

Soil and Plants

Rubidium has been identified in a number of different soil types, the content ranging from $1-15 \times 10^{-3}\%$, with a tendency to accumulation in the surface layers.[18-20] In some soils rubidium may be fixed by entering into the lattice of an illite-type clay mineral.[21] Rubidium is found to be present in a large number of species of plants.[22-28] In general, the average content of phanerogams[29,30] is about 18 mg. per kg. based on dry weight (18 p.p.m.) with a range of 1–98 mg. per kg. Cryptogams[31,32] average 120 mg. per kg. with a range of 2.4–2800 mg. per kg., the very high values being found in certain fungi.[33-36] Species growing in water or damp places may contain 3–7 times as much rubidium as species of the same family growing in dry places.[37,38] The rubidium contents of a large number of species of seeds have been determined and found to range from 0.6 mg. per kg. in rye to 46.7 mg. per kg. in coffee beans,[39-43] a higher content generally being present in seeds of crucifers than in those of labiates. Marine algæ concentrate rubidium to about 10 times the concentration normal in sea water,[44] while fresh water plants have much the same range of rubidium contents as the marine species, indicating that the element must be concentrated about a thousandfold by these plants.[45]

The uptake of rubidium by plants from soil is inversely proportional to the available potassium.[46,47] When the ratio of rubidium to potassium is 34 : 1000 milliequiv. the ash of the potato plant contains 1.1% of rubidium, 14% of that available being taken up. If, however, the rubidium is reduced to one hundredth, the plant takes up 43% of that available.[48] Metabolising barley roots rapidly accumulate rubidium from solutions of the order of 10^{-9} molar. Rubidium taken up when metabolism is suppressed is loosely held, being readily exchanged with the inert isotopes.[49] Absorption of rubidium by roots is inhibited in parallel with the inhibition of ascorbic acid oxidase, while potassium inhibits the uptake of rubidium but facilitates its transfer to the shoots.[50] Kinetic studies of the absorption of rubidium from solutions containing other ions indicate that potassium and caesium interfere competitively with rubidium uptake while lithium and sodium do not.[51,52] The uptake of rubidium is found to vary along the root, being highest about 2 mm. behind the tip and lowest in the succeeding 2–6 mm. where cell elongation is occurring most rapidly.[53,54] Little upward translocation occurs.[55] Mycorrhizal roots of the loblolly pine absorb less rubidium than non-mycorrhizal roots.[56] Rubidium chloride, in common with other alkali chlorides, causes calcium depletion in barley and wheat roots.[57] The uptake of rubidium by potato tuber tissue obeys a Freundlich equation and the results are consistent with combination of the metal with one or more constituents of the protoplasm.[58] In carrot discs also there appears to occur combination with some metabolic carrier.[59] In mung bean roots both calcium ions and ultra-violet radiation enhance the uptake of rubidium,[60] but *X*-radiation depresses the uptake.[61] Plant auxins also increase the uptake of rubidium by various plant tissues and the increase is related to increased hydration of the tissues.[62-64] The rates of penetration of potassium and rubidium into *Valonia* cells are proportional to their ionic radii.[65] Sorption of rubidium ions by wheat chloroplasts is very small.[66] The rate of movement of injected rubidium salts in the trunks of the white pine and the yellow birch ranges from an upward movement of one foot per minute in July to zero in October.[67]

Rubidium has been ascribed a role as an important trace element for potatoes[68] while the growth of many plants is stimulated by small percentages of the metal in the soil.[69] Most cereals appear to be indifferent to the presence of low concentrations of rubidium but are killed or rendered incapable of completing their development by higher concentrations.[70,71] Rubidium salts inhibit the growth of radish seedlings[72] and of the roots of rye[73] and of *Lepidium sativum.*[74] *Ankistrodesmus* develops resistance to the element after growth in solutions containing rubidium.[75] The toxic effect of rubidium to cereals is reduced when the concentration of potassium is increased.[76,77] A study of the amino acid distribution in plant tissues suggests that low concentrations of rubidium can offset the effects of potassium deficiency.[78] There is some evidence that rubidium influences the synthesis of amylase in germinating barley[79] and also restricts the uptake of phosphorus.[80] Respiration is increased in excised barley roots by rubidium sorbed on exchange resins.[81]

Animals

Rubidium has been identified by spectroscopy in many though not in all species of marine and terrestrial animals.[82,86] The contents range from 3–28 mg./kg. in invertebrates, 2–20 mg./kg. in fishes, batrachians and reptiles, 8–65.5 mg./kg. in mammals, and more than 100 mg./kg. in birds.[87] Human liver has been found to contain 14 mg./kg.[88] and this is not stored during foetal life but accumulated during the nursing period.[89] Rubidium appears to be a normal constituent of human blood, ranging from 1.63 to 4.95 mg. per l. in whole blood and 0.53 to 1.80 mg. per l. in serum, the difference being the intracellular content.[90,91] Rubidium is one of the least toxic of the alkali metals[92-94] and can in fact be substituted for potassium without affecting the respiration of erythrocytes.[95] Rubidium[86] has been found useful as a tracer for potassium for studying the rate of exchange between plasma and erythrocytes.[96] Both nucleated and non-nucleated erythrocytes are freely permeable to rubidium[97] which competes with potassium but not with sodium for transport into the cells.[98] The permeability of the cells to rubidium is greatly increased by carbon dioxide in the presence of a minute concentration of lead ions[99] (1 in 25 × 10^{-6}). The rate of excretion of rubidium from the blood is slow, 59 to 188 days being required for 50% of the initial content to be excreted in the urine,[100] this rate being about half that for potassium.[101] Estimates of the extracellular body space using labelled rubidium and potassium agree[102] reasonably well. Rubidium may also be completely substituted for potassium in maintaining the active transport of water and sodium ions through frog skin.[103]

Intravenous injection of rubidium chloride in man and animals causes a slight decrease in pH and a marked decrease in the surface tension of the blood.[104] Rubidium has a very similar effect to potassium on isolated organs.[105] Injections of rubidium chloride produce a fall in the blood pressure in the carotid artery[106] while contraction of the frog heart is decreased by rubidium chloride more intensely and more rapidly than by potassium chloride.[107-113] Rubidium ions are taken up by muscles which have contracted during perfusion but are not taken up by resting muscles and if taken up the ions are not removed by subsequently perfusing with potassium-Ringer solution.[114] Potassium may be replaced by rubidium in Ringer solution with no abnormal effects on the contraction of frog muscle but at a certain concentration of rubidium chloride double contractions occur.[115] Rubidium behaves like potassium in causing contraction and depolarisation of muscle, the effect being maximal in 0.1M rubidium chloride but only about 60% of that produced by the same concentration of potassium chloride.[116-119] The injury potential of snail muscle is lowered by rubidium ions.[120] Rubidium, like potassium, stimulates nerves by causing depolarisation[121-124] and the mechanism of depolarisation by these two ions is different from that caused by sodium or ammonium ions.[125] There is a linear relationship between the lowering of the membrane potential of amphibian nerve and the logarithm of the external rubidium concentration.[126] Rubidium ions cause reversible abolition of the action current, which may be prevented by calcium ions,[127] and also liberate acetylcholine from innervated ganglia.[128] Rubidium differs from potassium in increasing the anelectronic potentials of spinal root nerves whereas potassium decreases the potentials.[129] The chemoreceptors of the frog palate are stimulated by rubidium to about the same degree as by potassium.[130] Rubidium is 8 times as active as potassium in causing contractions of the pig uterus.[131] Violent excitation followed by paralysis is the result of intracerebral injection into the frog.[132] The anaesthesia caused by magnesium salts is instantly relieved by injection of rubidium salts almost as effectively as by potassium.[133] The crop of *Aphysia* is contracted by rubidium salts[134] and the metamorphosis of *Triton* larvae is delayed by rubidium much more than by potassium or sodium.[135]

Solutions of rubidium chloride injected into dogs cause an increase in the volume of the kidneys.[136] The chloride also stimulates the respiratory centre causing an increase in the rate of breathing.[137] Rubidium affects the respiration of brain tissue in the same manner as potassium, the effect of both metals being different from that of sodium.[138] Rubidium also increases the respiration of rat-liver mitochondria in the presence of Krebs-cycle intermediates[139] and maintains the motility of ram and bull spermatozoa.[140]

Rubidium ions cause a decrease in the respiration of neoplastic and embryo

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cells;[141,142] while the growth of embryos and some tumours is inhibited,[143,144] other types of tumour are unaffected.[145] The uptake of rubidium ions by tumour tissue is much greater than by normal tissue and brain tumours may contain 6–19.3 times more rubidium than normal,[146-148] but this does not seem to be true for benzopyrene-induced tumours in rats.[149]

Rubidium stimulates glycolysis by *Lactobacillus arabinosus* cells and also by cell-free extracts, the action being presumed to be on the cell membrane.[150] The ion also stimulates the acetate-activating enzyme,[151] pyruvic phosphoferase of erythrocytes[152] and activates tryptophanase.[153] Urease,[154] broad bean peroxidase[155] and plant carbonic anhydrase[156] are however inhibited.

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CHAPTER 5

CÆSIUM

SECTION LXXX

THE OCCURRENCE OF CÆSIUM

By P. C. L. THORNE AND K. W. ALLEN

Caesium has been found in the fumarole sublimation products from the crater of Vesuvius,[1] with 11·5% of caesium in the water-soluble portion. Here also is found avogadrite,[2] which is KBF_4 with associated isomorphous $CsBF_4$ (9·5%). A caesium biotite, biaxial, with α 1·573, β 1·620, γ 1·620, d 3·10 and containing 3·14% Cs_2O has been found in South Dakota,[3] and a similar biotite in the Ilmen Range in the Urals.[4] The occurrence of caesium has also been reported in other places in the U.S.S.R.[5-10] but the content of the element reported is very low, although several Kazakhstan pegmatites contain 0·1–0·4% Cs. Sources in Australia,[11] Switzerland[12] and Arizona[13] have also been noted. The presence of some caesium is typical of rose beryl and it is suggested that this element is the colouring agent.[14] Caesium has been found in arable soils[15] (0·3–25·7 mg. per kg.), in both phanerogams and fungi[16] (mean content, 22 mg. per kg. of dried tissue) and also in animals, especially invertebrates.[17] In sea water, 3·4–4·3 × 10^{-6} g. per l. has been found around the Japanese coast.[18]

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SECTION LXXXI

THE PREPARATION AND USES OF CÆSIUM

By J. P. QUIN

THE PREPARATION OF CÆSIUM

When Mellor wrote the original Treatise, metallic cæsium was a chemical curiosity which had been prepared only in very small amounts by the thermal reduction of cæsium compounds with calcium, aluminium or magnesium. No work appeared to have been carried out on the preparation of the metal by the electrolysis of solutions of cæsium compounds in non-aqueous solvents, or of cæsium compounds in the fused state (Mellor,II,447-450). Since then considerably more information has been accumulated on the formation and preparation of the metal, but the demand for cæsium still remains very small.

Like rubidium, cæsium metal is not manufactured on a commercial scale, although it has some applications in industry. In 1946 the world output of cæsium in the form of ore was estimated to be about 10 lb.[1] and in 1949 the production of cæsium metal in the United States was estimated to be 1 lb, with a potential production of about 1 ton.[2] In 1953 the U. S. output was given as 25 lb.[2a] No later figures appear to be available, but the production is evidently very small. It may be mentioned that mixtures of rubidium and caesium are frequently marketed as cæsium metal.[3]

Preparation of Cæsium by Chemical Reaction.

In general the methods of formation and preparation of sodium by chemical means are equally applicable to caesium (see pages 308,324), so that its preparation chemically involves either the thermal reduction of caesium compounds or the reduction of caesium compounds with metallic or non-metallic reducing agents at high temperatures.

Thermal Decomposition of Cæsium Compounds.

Cæsium is formed by thermal decomposition of cæsium azide in vacuo.[4-7a] It is necessary to heat the azide to 350°C. to initiate the decomposition which is then carried out at 390°C. over a period of three or four days. A yield of about 90% is obtained and it is claimed that the metal so produced is very pure and completely free from gaseous impurities.[4] The grey residue remaining after the decomposition yields a considerable amount of ammonia on treatment with water, indicating that some cæsium nitride has been formed.[7] The method has the disadvantages that it is slow and that cæsium azide tends to decompose with explosive violence under certain conditions.[8]

The formation of cæsium by the thermal decomposition of cæsium cyanate, ferrocyanide or ferricyanide has been discussed.[8]

Reduction of Cæsium Compounds with Metallic or Non-metallic Reducing Agents.

The preparation of cæsium by heating a suspension of carbon in molten cæsium hydroxide while passing a stream of inert gas through the melt, and then removing from the gas the cæsium vapour produced, has been patented.[8a]

Cæsium is formed in about 75% yield when a mixture of cæsium chloride and calcium carbide is heated in vacuo at 700–800° C.[9]

It has been proposed to pass the vapour of the chloride in vacuo over solid calcium carbide at a temperature preferably between 800–1100°C., and condense the cæsium vapour so produced.[9a]

Metallic cæsium may be prepared by the reduction of cæsium chromate with aluminium. In one method an aluminothermic reduction is effected with a pelleted mixture of cæsium chromate, chromic oxide and powdered aluminium.[10] The chromic oxide is useful in giving on reduction a large amount of excess heat. Sufficient aluminium is used to reduce completely both the cæsium chromate and the chromic oxide. On heating the pellets an exothermic reaction which results in the quantitative formation of cæsium is initiated and the method has been used for the preparation of cæsium in situ in photoelectric cells.

Cæsium can also be conveniently prepared by the reduction of cæsium compounds with alkaline earth metals such as barium or calcium. In one such method a small quantity of a mixture of cæsium chloride with a solution of barium azide is evaporated to dryness at room temperature and then heated in vacuo.[11] The barium azide decomposes at a temperature between 100° and 200°C., and the barium metal so formed then reduces the cæsium chloride to give cæsium which distils off at a temperature between 250° and 350°C. At this comparatively low temperature no trouble arises from the distillation of barium. It is essential to carry out the evaporation to dryness at room temperature, as at higher temperatures considerable hydrolysis of the barium azide to barium hydroxide occurs and this reduces the yield of cæsium.

A satisfactory method of preparing cæsium in moderate quantities in the laboratory is that due to Hackspill whereby cæsium chloride is thermally reduced with calcium in vacuo to give cæsium according to the equation:-[8,12-18]

$$2CsCl + Ca \rightarrow CaCl_2 + 2Cs.$$

When an intimate mixture of cæsium chloride and metallic calcium is heated at 675°C. under a pressure of 0·001 mm. of mercury, the reduction proceeds readily and quietly and cæsium distils off and is collected in a glass receiver. On redistillation in vacuo very pure metal is obtained in a yield of 90%.[15] One sample of cæsium made in this way was examined spectrographically for purity and found to contain only a trace of sodium.[17] A number of workers have used this method with minor modifications for the preparation of small amounts of pure cæsium and detailed descriptions are available of the apparatus and technique employed.[12-18] The reduction has also been carried out by heating a mixture of cæsium bromide and calcium metal in vacuo at 600–700°C.[19]

To obtain cæsium in a form which can be easily handled without oxidation, it has been proposed to carry out the reduction of a cæsium salt with calcium and then to alloy the cæsium with a metal such as lead, tin, zinc, cadmium, silver, strontium, barium or magnesium, from which cæsium can be readily separated by distillation.[20,21]

According to a patent, the reduction of cæsium compounds with calcium can also be applied to the production of the metal directly from its ores.[22,23] Thus pollucite, containing 35% of cæsium oxide as a silicoaluminate, is heated at 900°C. for several minutes to remove water, after which 30 g. of calcium and 10 g. of pollucite are heated together in vacuo. The reduction starts at 750°C. and is completed at 900°C. Cæsium distils from the reaction mixture as a crude metal which, by subsequent vacuum distillation, may be freed from alkaline earth metals and alkali metals other than rubidium. The yield of pure cæsium is 2·4 g.[23]

It has also been proposed to prepare cæsium by the reduction of cæsium chloride with metallic cadmium.[35]

Cæsium may be prepared by reducing cæsium compounds with iron at high temperatures and low pressures.[24,25] This reaction proceeds more readily than the corresponding reactions with sodium or potassium compounds, provided that it is carried out in vacuo and at such a temperature that the vapour pressure of the alkali metal is not greater than 1 cm. of mercury. Reduction takes place rapidly at the melting point of the cæsium compound.

When cæsium hydroxide is heated with excess of iron under a reduced pressure of 0·001 mm. of mercury, a slight evolution of hydrogen indicates the start of the reduction at a temperature between 500 and 550°C. At 700°C. cæsium distils off readily:-

$$6CsOH + 4Fe \rightarrow 2Fe_2O_3 + 3H_2 + 6Cs.$$

The yield of metal, however, does not exceed 50% owing to reaction between cæsium hydroxide and the iron oxide produced during the reduction forming a ferrite which is not readily reduced under the conditions of the experiment.

With cæsium sulphate, reduction with iron in vacuo starts about 700–800°C. with a slight evolution of oxygen and sulphur dioxide, and proceeds rapidly at 1000°C. with the evolution of cæsium vapour. At 1100°C. an 80% yield of cæsium is obtained, but the metal is partially oxidized by the gases evolved during the reaction. With cæsium carbonate and excess of iron in vacuo, evolution of gas starts at about 650°C. and continues up to about 1000°C. At this latter temperature cæsium vapour distils off in about 50% yield, but again the metal is obtained in a slightly oxidized condition. The reaction between cæsium nitrate and excess of iron under similar conditions starts at 500°C. with the evolution of a gas containing 10% of oxygen and 90% of nitrogen and at 600°C. a 10% yield of cæsium is obtained. Analysis of the residue left after completion of the reaction indicates that the reaction proceeds according to the equation:-

$$2CsNO_3 + 4Fe \rightarrow 2Fe_2O_3 + N_2 + 2Cs.$$

The corresponding reaction with cæsium chloride is ineffective because ferrous chloride and cæsium distil over together and react to reproduce iron and cæsium chloride.[25]

A process has been patented for reducing cæsium chloride with a rare-earth metal alloy such as mischmetall.[26] A mixture of cæsium chloride and mischmetall is placed in a glass vessel which is then evacuated to a pressure of less than 0·001 mm. of mercury and heated to about 270°C. or higher to remove occluded gases. Then the mixture is heated electrically in the evacuated vessel to effect reduction.

The reduction of cæsium permanganate or dichromate with silicon containing small amounts of aluminium to give cæsium metal has been patented.[27]

The reduction of cæsium compounds with zirconium has been studied.[28-31] Zirconium has the advantage of being almost completely non-volatile, and by choosing a suitable cæsium compound it is possible to ensure that the only volatile product of the reaction is metallic cæsium. The method is recommended for the preparation of small amounts of cæsium in the laboratory.

Cæsium bisulphate and zirconium powder in the proportions 1:5, when heated in vacuo to about 550°C., react explosively, and whilst the evolved cæsium vapour condenses on the colder parts of the apparatus as a shining deposit in a yield of 70–97%, it is contaminated with non-volatile reaction products and unchanged zirconium carried over by the explosion. Cæsium sulphate and zirconium mixed in the proportions 1:2 and 1:4 also react explosively at about 550°C. to give a 50% yield of cæsium containing about 15% of oxide and 10% of sulphide, but 1:10 and 1:25 mixtures react smoothly at temperatures between 500° and 600°C. under similar conditions (though the former may explode on rapid heating), giving cæsium free from oxide and sulphide.[29]

Cæsium dichromate and zirconium in the proportions 1:4 react explosively at about 320°C. in vacuo, whereas a 1:10 mixture evolves cæsium smoothly at about 380°C. and 1:20 and 1:40 mixtures react smoothly at 500°C. With coarse zirconium powder the yield of cæsium is about 20%, but the product contains 10% of oxide. When the reduction is carried out under similar conditions using a finer grade of zirconium powder the oxide content of the product is reduced, and when 1:20 and 1:40 mixtures are used cæsium free from oxide is obtained.[29]

The reaction of cæsium chromate with zirconium requires considerably higher temperatures: thus, cæsium chromate and zirconium in the proportions 1:2 react smoothly in vacuo at 725°C., and the yield of cæsium is about 50%, with an oxide content of 10%. Using a 1:4 mixture, heated to 1000°C., a 90–96% yield is obtained of cæsium substantially free from oxide contamination.[29]

Cæsium halides are unsuitable for use in this way because of the comparative volatility of the zirconium halide formed in the reaction.[29]

A number of patents have been taken out for the preparation of cæsium in situ in electrical discharge devices.[31-35]

ELECTROLYTIC PREPARATION OF CÆSIUM

Little attention appears to have been given to the preparation of cæsium by the electrolysis of cæsium compounds either in solution in non-aqueous solvents or in the fused state.

According to a patent cæsium is prepared by the electrolysis of a non-aqueous liquid comprising anhydrous liquid ammonia, methylamine, ethylamine, pyridine or mixtures of these liquids, containing a solution of a cæsium salt such as the perchlorate or thiocyanate. Iron, copper or carbon is used for the cathode and carbon is the preferred material for the anode.

The concentration of the cæsium salt in the anhydrous liquid must be at least 2g.-mol./litre. The cæsium is deposited as a colloid, suspension, paste or metal depending on the concentration of the cæsium salt in the electrolyte. It is claimed that the deposited cæsium can be readily separated from the electrolyte and obtained in a high degree of purity by evaporation of any excess solvent.[35a]

The Ewan process, whereby an alkali metal is prepared by the electrolysis of a solution of an alkali metal salt in liquid ammonia in the presence of an alkali metal amalgam anode, has been proposed for the preparation of cæsium.[37] The preparation of cæsium by extracting the metal from cæsium amalgam by inert solvents, followed by recovery of the cæsium by evaporation of the solvent, has been considered.[38-38b] According to a patent the efficiency of electrolysis of fused alkali hydroxides, including fused cæsium hydroxide, may be increased by the addition of the corresponding amide to the fused electrolyte (see page 337). Similar results may be obtained when cæsium nitrate is electrolyzed in the presence of auxiliary salts such as cæsium amide or cæsium carbonate.[36]

A miniature cell for the preparation of small amounts of alkali metals by electrolyzing their fused salts has been described, and it has been suggested that the cell may be suitable for the preparation of metallic cæsium, although this has not actually been attempted.[39] In this connexion it may be recalled that Kirchhoff and Bunsen stated in 1862 that cæsium could not be prepared by the electrolysis of fused cæsium chloride.[40] Similar results were obtained by Setterberg, who nevertheless succeeded in obtaining the metal by electrolyzing a fused mixture of 4 parts of caesium cyanide and one part of barium cyanide, using aluminium electrodes.[41]

An electrolytic method for preparing cæsium metal in discharge tubes has been described,[42] and a patent describes the coating of electrodes in discharge tubes with alkali metals such as cæsium by the gaseous electrolysis of a vaporized compound.[43]

PURIFICATION OF CAESIUM

Cæsium is readily purified by distillation, preferably in vacuo, and the necessary procedure, with a detailed account of the apparatus required, has been described by a number of authors.[7a, 44–50] The distillation may be conveniently performed in Jena glass apparatus.[48] The purification of cæsium by treating the metal with molten cæsium chloride or other inert salts has also been discussed.[51]

HANDLING AND STORAGE OF CAESIUM

The handling and storage of cæsium have been discussed.[52] Cæsium may be handled like the other alkali metals provided allowance is made for the fact that the metal is extremely reactive and ignites spontaneously in air or dry oxygen at room temperature. Storage in the absence of air is therefore essential.[52] Even when cæsium is stored in highly evacuated glass tubes the traces of air that are always present react slowly with the metal which gradually acquires a golden yellow colour, and if more air is present the metal rapidly becomes black. An elegant method has, however, been devised whereby the metal can be stored for long periods and its characteristic silvery appearance maintained. Cæsium is distilled at a pressure of 0·001 mm. of mercury into the first of two glass bulbs connected by a constricted tube and there sealed off. After it has remained in the apparatus for several months and removed all traces of moisture and gases from the interior the metal is distilled into the second bulb which is then sealed off at the constriction.[12]

A technique for the preparation of samples of cæsium suitable for the determination of physical properties has been described.[12a] The preparation of colloidal solutions of cæsium has been discussed.[12b,c] The toxicity of cæsium is said to be low.[12d,e]

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THE USES OF CAESIUM

The uses of metallic cæsium are very limited indeed and the quantities of the metal involved are very small. Cæsium may be used to eliminate the last traces of oxygen from vacuum tubes and to obtain a high vacuum in radio valves.[1-3] It is also employed in photoelectric cells, as the sensitivity of cæsium is particularly strong in the range of visible light so that cæsium cells are useful in measuring accurately the intensity of that light which is of the greatest practical interest.[4,6] Such cæsium cells have found application in photometry, in television, in sound cinematography and in controlling motor car headlights.[1-9] It has been proposed to use cæsium in a cæsium vapour rectifier and for some purposes this is said to offer certain advantages over a mercury vapour rectifier.[4]

Cæsium has been used in the manufacture of image storage screens[11] and gas-filled thyratrons,[12] and to facilitate the study of grain growth in steel by emission electron microscopy.[13] The use of radioactive cæsium isotopes in industry and medicine has been discussed.[14] ^{137}Cs with a half-life of 33 years can be used in the preservation of foods,[15] in the detection of defects and misalignment of parts[16] and in scintillation spectrometry.[17]

It has also been proposed to use cæsium as a constituent of alloys.[10]

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SECTION LXXXII

THE PHYSICAL PROPERTIES OF CAESIUM

By W.H. WILSON

Structure, Atomic and Ionic Radii Etc.

Caesium crystallises as a body-centred cube – at least at low temperatures.[1-6] Lattice constant measurements have given 6·05 A. at −170°C.,[1,2] 6·067 A. at −100°C.,[6] and 6·13 A. at −10°C.[3] These figures correspond to atomic radii of 2·62–2·65 A.

Barrett[7] cooled specimens of 98·7% caesium to 1·2°K. and then examined them metallographically at 0°C. in a search for a spontaneous martensitic transformation similar to that found with lithium and sodium at low temperatures (see Volume II, Supplement II, pages 32 and 377). All the caesium surfaces were, however, devoid of transformation markings.

Small breaks in the plots of electrical resistance and thermoelectric power against temperature were observed by Bidwell[8] in the region of −80°C. and were assumed to indicate a transformation from a crystalline form to an amorphous form.

Diffraction of *X*-rays by liquid caesium has been studied by Randall and Rooksby[9] who found an intensity peak at $(\sin \theta)/\lambda = 0·111$.

Theoretical treatments of the cohesion in metallic caesium have been given by several authors[10-12] who have calculated the solid-state parameters by methods similar to those applied to the other alkali metals (see Volume II, Supplement II, page 380 and this volume, page 2144.

Various attempts have been made to establish sets of ionic radii from which interionic distances in crystals can be obtained by summation.[13-15] On the basis of the experimental interionic distances in NaF, KCl, RbBr, CsI and Li_2O, Pauling[13] constructed a set of ionic radii in which the caesium ion had a value of 1·69 A., values for the other alkali ions being Li^+, 0·60 A.; Na, 0·95 A.; K^+, 1·33 A.; and Rb^+, 1·48 A. Goldschmidt[14] in an earlier treatment gave 1·65 A. for the radius of the Cs^+ ion.

Density

At 18°C. the density of solid caesium has been reported as 1·8920.[16] Low temperature measurements[17] have given densities of 2·09 at 77°K. and 2·13 at 4·2°K. From *X*-ray measurements the density at 100°K. has been given as 1·98.[1] Calculation of the density and atomic volume at 0°K. has been discussed by Herz.[18]

The density of liquid caesium at its melting point (28·4°C.) has been measured as 1·841.[19]

The increase in volume on fusion was reported by Losana[16] as 2·66%. Measurements of the volume increase on fusion at pressures up to 4,000 kg./cm.^{2} have given the following figures:[20,21]

Pressure, kg./cm.^{2}	1	500	1000	1500	2000	2500	3000	3500	4000
ΔV, cm.^{3}/g. $\times 10^2$	1·36	1·18	1·05	0·96	0·88	0·83	0·78	0·75	0·72

Mechanical Properties

As part of his extensive work on the physical properties of substances at high pressures, Bridgman[20-29] has studied the compression of cæsium at pressures up to 100,000 kg./cm.^{2} Table I is based on his more recent measurements.[25,26]

TABLE I.- EFFECT OF PRESSURE ON THE VOLUME OF CAESIUM AT ROOM TEMPERATURE

Pressure, kg./cm.^{2}	Relative Volume
0	1·000
2,500	0·900
5,000	0·841
10,000	0·761
15,000	0·702
20,000	0·656
25,000	0·609
30,000	0·571
40,000	0·521
50,000	0·431
60,000	0·409
70,000	0·392
80,000	0·381
90,000	0·375
100,000	0·368

Fig. 1 compares the compressions of the five alkali metals and it is apparent that caesium is the most compressible.

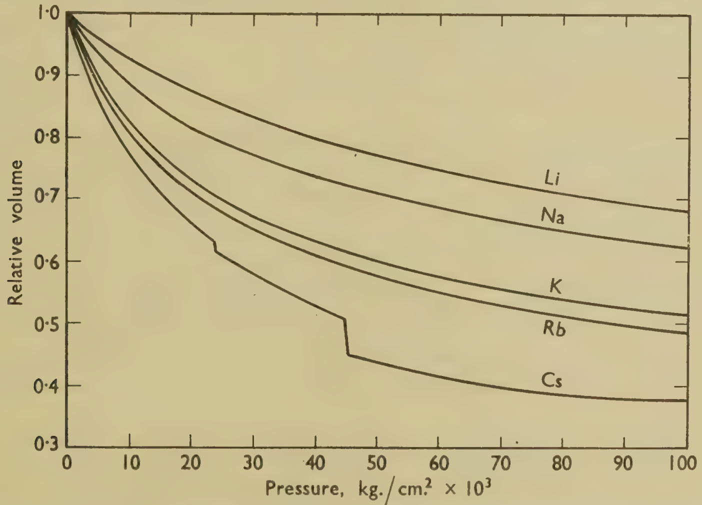

FIG. 1.- EFFECT OF PRESSURE ON THE VOLUMES OF THE ALKALI METALS AT ROOM TEMPERATURE

Two reversible volume discontinuities occur with cæsium at pressures of 23,300 kg./cm.^{2} and approximately 45,000 kg./cm.^{2} For the first, the volume (relative to that at zero pressure) changes from 0·6284 to 0·6224; for the second it changes from 0·498 to 0·442, a volume change of ~11%. Both discontinuities show the clean-cut characteristics usually associated with a phase change. The first corresponds most probably to a change from a body-centred cubic structure to the more closely packed structure of a face-centred cube. Such a change of lattice at about this pressure was indicated by calculations carried out by Bardeen[30] before the experimental observation. The second transition, with its very large volume change, has been attributed to a rearrangement in the electronic shells of the atom.[31,32]

At 4·2°K. the values of Table II have been obtained for the relative volume of caesium at pressures up to 10,000 atmospheres[17] (1 atmosphere = 1·033 kg./cm.^{2}).

TABLE II.- EFFECT OF PRESSURE ON THE VOLUME OF CAESIUM AT 4·2°K.

Pressure, atm.	Relative Volume
0	1·000
500	0·978
1,000	0·956
1,500	0·937
2,000	0·919
3,000	0·887
4,000	0·859
6,000	0·812
8,000	0·771
10,000	0·737

Bridgman[20] gave the initial compressibility of caesium at 50°C. as 70 × 10^{-12} cm.^{2}/dyne. More recent values[17] for the initial compressibility at low temperatures are 48·7 × 10^{-12} cm.^{2}/dyne at 77°K. and 43·5 × 10^{-12} cm.^{2}/dyne at 4·2°K.

From measurements of the velocity of ultrasonic waves in liquid caesium (page 2314) the adiabatic compressibility of the liquid metal at its melting point is 58·1 × 10^{-12} cm.^{2}/dyne; the isothermal compressibility at the same temperature is 67·3 × 10^{-12} cm.^{2}/dyne.[33]

Surface Properties and Colloidal Cæsium

There appear to have been no experimental determinations of the surface tension of cæsium, but by the use of general empirical relationships between surface tension and other physical properties an estimate of 55 dynes cm.$^{-1}$ has been made for the surface tension at the melting point.[34] A consideration of the co-ordination numbers of atoms at the surface and in the bulk of the liquid has led to a value of 78 dynes cm.$^{-1}$ for the surface tension.[35] Values calculated for the surface tension of cæsium in various wave mechanical treatments[36-39] have shown wide variations (40 to 110 dynes cm.$^{-1}$): the treatment[39] that gave the best agreement with experiment for lithium, sodium and potassium (q.v.) gave 40 ergs cm.$^{-2}$ for the surface tension of cæsium at its melting point.

From surface tension data for fused salts a value of 150 has been calculated for the atomic parachor of cæsium.[40] The same value was obtained by extrapolation from the straight line plot of the logarithm of the atomic number against the logarithm of the parachor for the other alkali metals.[41]

Cæsium dispersions may be prepared by the method that has been widely used with sodium (Volume II, Supplement II, page 386), namely by agitating the molten metal with the dispersion medium and continuing agitation until the dispersion has been cooled below the melting point of the metal.[42] Dispersions in mineral oil have been used above the melting point of the metal without coagulation.[42]

Colloidal solutions of cæsium have been prepared by condensation methods, the metal and the dispersion medium being evaporated in vacuum and the mixed vapours condensed on a surface cooled with liquid air.[43,44] Cæsium sols in ether prepared in this way by Tomashevskii had a dark blue colour and were stable for only twenty minutes.[44]

Viscosity

Viscosity values for cæsium obtained by an oscillating sphere method are shown in Table III.[19]

TABLE III.- VISCOSITY OF CAESIUM

Temperature, °C.	Viscosity, millipoise
28·4	6·837
43·4	6·299
99·6	4·753
140·5	4·065
168·0	3·750
210·9	3·343

The data have been represented by the following equations:

$$\eta = 10{\cdot}14 \times 10^{-4} e^{576/T}$$

$$\text{and } \eta v^{1/3} = 1{\cdot}029 \times 10^{-3} e^{277/vT}, \text{ (v is the specific volume)}$$

The latter, which makes allowance for the change of volume with temperature, gives slightly the better fit.

Melting Point and Heat of Fusion

Using pure caesium obtained by thermal decomposition of cæsium azide and purified by vacuum distillation, Clusius and Stern[45] obtained a value of 28·64 ± 0·17°C. for the melting point. Melting point values obtained by other workers on samples of cæsium that were being used for the determination of other physical properties have included 29·7°C.,[20,21] 28·8°C.,[16] 28·0°C.,[19] and 27·4°C.[8] The last value was obtained with a sample reported to contain a trace of sodium.

Increase of pressure raises the melting point; determinations at pressures up to 135 atmospheres have given:[16]

Pressure, atm.	1	50	100	135
m.p., °C.	28·8	30·0	31·5	32·5

Other measurements at higher pressures have led to the following values:[20,21] (1 atmosphere = 1·033 kg./cm.^{2}).

Pressure, kg./cm.^{2}	m.p., °C.
1	29·7
500	41·4
1000	51·9
1500	61·4
2000	70·2
2500	78·3
3000	85·7
3500	92·4
4000	98·5

The pressure variation of melting point for caesium is compared with that for the other alkali metals in Fig. 2.

A value of 520·1 g.-cal./g.-mole (equivalent to 3·92 g.-cal./g.) was obtained for the heat of fusion of cæsium by Clusius and Stern:[45] this agrees

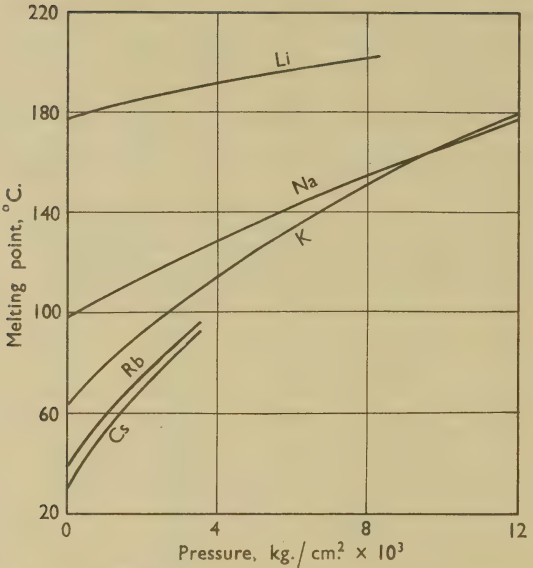

FIG. 2.- THE MELTING POINTS OF THE ALKALI METALS AS A FUNCTION OF PRESSURE

fairly well with much earlier values[46,47] of about 3·8g.-cal./g.

Application of the Clapeyron equation to experimental data on the variation of melting point with pressure and the volume change on fusion has shown the latent heat of fusion to increase from its value of about 3·9g.-cal./g. at atmospheric pressure to about 5·4g.-cal./g. at a pressure of 4000 kg./cm.^{2}.[20,21]

Vapour Pressure, Boiling Point and Degree of Association

Several experimental methods have been used to determine the vapour pressure of caesium.

Scott[48] using a vibrating quartz manometer made measurements between 50°C. and 115°C. which he represented by the equation

$$\log p \text{ (mm.)} = -3753/T + 7{\cdot}256$$

When a tungsten filament is raised to a temperature higher than 1200°K. in saturated caesium vapour, the caesium atoms striking the filament are ionised, and the positive ion current passing to a negatively charged cylinder surrounding the filament gives a measure of the vapour pressure.[49-52] Taylor and Langmuir[52] used this method at temperatures from −35°C. to +73°C. and represented the vapour pressure of solid caesium by the equation;

$$\log_{10} p \text{ (mm.)} = -4150/T + 10{\cdot}5460 - 1{\cdot}00 \log_{10} T$$

and that of liquid caesium by:

$$\log_{10} p \text{ (mm.)} = -4041/T + 11{\cdot}0531 - 1{\cdot}35 \log_{10} T$$

The equations were considered to be accurate to within 1% from 220°K. to 350°K., within 3% up to 600°K., and within about 8% at 1000°K.

The absorption of caesium spectral lines in caesium vapour has been used to obtain relative values for the vapour pressure between 190°C. and 230°C.[53,54]

There have been several reviews of vapour pressure data for caesium.[55-58]

Ditchburn and Gilmour[58] in 1941 considered the results of Taylor and Langmuir[52] to be the most reliable. They adopted equations differing slightly (by 1% at 300°K. and by 4% at 250°K.) from those of Taylor and Langmuir in order to fit thermal data more accurately. For the solid they gave:

$$\log_{10} p\ (\text{mm.}) = -4120/T + 10{\cdot}446 - 1{\cdot}0\log_{10} T$$

(within 2% between 275° and 299°K.;
10% between 240° and 299°K.)

and for the liquid:

$$\log_{10} p\ (\text{mm.}) = -4042/T + 11{\cdot}176 - 1{\cdot}4\log_{10} T$$

(within 2% between 299° and 350°K.;
10% between 299° and 650°K.)

Temperatures at which the vapour pressure assumes rounded values as calculated from the equations of Ditchburn and Gilmour are given in Table IV.[58]

TABLE IV.- VAPOUR PRESSURE OF CAESIUM

Pressure, mm. Hg	T, °K.
10^{-7}	274
10^{-6}	295
10^{-5}	319
10^{-4}	348
10^{-3}	383
10^{-2}	426
10^{-1}	480
10^{0}	551
10^{1}	(650)

No vapour pressure measurements have been made at high pressures and the value in parentheses is extrapolated. Further extrapolation leads to a value of 985°K. for the boiling point. From other vapour pressure equations a boiling point of 958°K. has been deduced.[59]

Values, calculated from spectroscopic data, of the dissociation constant of diatomic caesium vapour into atoms are given in Table V[60] (partial pressures in atmospheres).

TABLE V.- DISSOCIATION CONSTANT FOR DIATOMIC CAESIUM VAPOUR

T, °K.	$\text{Log } K = \text{Log } P^2_{\text{Cs}}/P_{\text{Cs}_2}$
273·16	−5·062
298·16	−4·345
400	−2·340
600	−0·363
800	+0·637
1000	+1·243
1200	+1·650
1400	+1·942
1500	+2·060

From spectroscopic data, the dissociation energy, Do^0, of the cæsium molecule is 0·45 e.V. or 10·4 kg.-cal./g.-mole.[61-64] The U.S. Bureau of Standards Selected Value[65] for the heat of formation of the gaseous Cs_2 molecule at 298·16°K. is 27·0 kg.-cal./mole. Values for the heat and free energy of formation of diatomic caesium vapour from the monatomic vapour are included in Table IX (page 2303).

Heats of Vaporisation and Sublimation

By the use of data from various sources, Kelley[66] has obtained the following equations for the heat of vaporisation and the free energy of vaporisation of caesium:

$$\Delta H(\text{kg.-cal./g.-atom}) = 19{\cdot}240 - 3{\cdot}03 \times 10^{-3}T$$
$$\Delta F(\text{kg.-cal./g.-atom}) = 19{\cdot}240 = 6{\cdot}98 \times 10^{-3}T \log T - 4{\cdot}080 \times 10^{-2}T$$

These give at the boiling point (which Kelley takes as 963°K.) $\Delta H_{963} = 16{\cdot}322$ kg.-cal./g.-atom and $\Delta S_{963} = 16{\cdot}95$ g.-cal./g.-atom, whilst $\Delta H_{298{\cdot}1} = 18{\cdot}337$ kg.-cal./g.-atom and $\Delta F_{298{\cdot}1} = 12{\cdot}227$ kg.-cal./g.-atom.

For the heat and free energy of sublimation Kelley[66] has given the equations:

$$\Delta H(\text{kg.-cal./g.-atom}) = 18{\cdot}740 + 3{\cdot}01 \times 10^{-3}T - 9{\cdot}1 \times 10^{-6}T^2$$
$$\Delta F(\text{kg.-cal./g.-atom}) = 18{\cdot}740 - 6{\cdot}93 \times 10^{-3}T \log T + 9{\cdot}1 \times 10^{-6}T^2 - 7{\cdot}40 \times 10^{-3}T$$

These lead to $\Delta H_{298{\cdot}1} = 18{\cdot}828$ kg.-cal./g.-atom, $\Delta F_{298{\cdot}1} = 12{\cdot}231$ kg.-cal./g.-atom and $\Delta S_{298{\cdot}1} = 22{\cdot}13$ g.-cal./g.-atom.

The U.S. Bureau of Standards Selected Values[65] for the heats, free energies, and entropies of vaporisation and sublimation are based on the above equations of Kelley.

Other more recent calculations[59] – but still based on much older vapour pressure data – have given the heat of sublimation to monatomic and diatomic gases at 298°K. as 18·67 kg.-cal./g.-atom and 26·63 kg.-cal./g.-atom respectively. At the boiling point (958°K.) the heat of vaporisation to the equilibrium vapour is given as 15·75 kg.-cal./g.-atom.[59]

Adsorption

In the presence of caesium vapour a strongly adsorbed film of caesium is formed on hot filaments of such metals as tungsten, nickel and molybdenum.[49,50] Adsorption of caesium on tungsten and the nature of the adsorbed films have been the subjects of extensive investigations.[49-51,67-83] The fraction, θ, of the tungsten surface covered with caesium has been studied as a function of pressure and temperature,[68,77] and measurements have been made of the rate of evaporation of caesium atoms, caesium ions, and electrons from these surfaces.[49-51,67,68,72,77]

At low filament temperatures all the caesium atoms striking the surface accumulate there until the surface is practically covered.[68,77,82] For low values of θ, caesium is adsorbed on tungsten as ions; with increasing coverage of the surface the ratio of adsorbed atoms to adsorbed ions increases.[70,79,80] The rate of evaporation of atoms at a given temperature increases with increasing coverage, whereas evaporation as ions is a maximum at about $\theta = 0{\cdot}01$ and thereafter decreases with increasing coverage.[68,77] On increasing the temperature sufficiently for the filament to be practically clean, all the caesium atoms on the filament are ionised and evaporate as such. Under these conditions (above about 1200°K.) all caesium atoms striking the filament are ionised (see pages 2298 and 2308).

The adsorbed caesium lowers the work function of the surface, the lowering at small values of θ being proportional to the number of atoms adsorbed.[68,74,77] As a result of the reduced work function the thermionic emission from a caesium-covered tungsten surface is much greater than from a clean tungsten filament.[49,51,67,68,72,77,84] For example, the electron emission from a tungsten filament at 700°K. increases by a factor of about 10^{25} when it is surrounded by caesium vapour at room temperature.[51,82] Taylor and Langmuir[72,77] found that the electron emission and the lowering of work function had maximum values at $\theta = 0\cdot67$. For this coverage the work function has dropped from the value of 4·62 e.V. for clean tungsten to 1·70 e.V.[77]

Cæsium is more strongly adsorbed on a tungsten surface that is partly covered with oxygen than on a clean tungsten surface, and the work function of a W–O–Cs surface is lower than that of W–Cs despite the fact that adsorption of oxygen alone on a tungsten surface raises the work function.[51,67,68,71] Because of the lower work function and because the more tightly bound cæsium permits the use of higher temperatures without serious loss of cæsium by evaporation, much greater electron emissions are attainable with W–O–Cs surfaces than with W–Cs. In order to achieve the high electron emission from W–O–Cs surfaces it is first necessary to activate tungsten surfaces that have been exposed to oxygen and to cæsium vapour by heating for several seconds at a temperature of about 1600°K.[84,85] This allows rearrangement of the atoms so that oxygen and cæsium are adsorbed on the tungsten surface next to each other.

Several reviews have appeared of adsorption and electron emission phenomena associated with W–Cs and W–O–Cs surfaces.[81-83,86] Photoelectric emission is dealt with on page 2310.

Adsorption of cæsium on calcium fluoride films gives rise to interlamellar swelling of the calcium fluoride.[87,88] The optical absorption of cæsium adsorbed on calcium fluoride has been studied (page 2312).

Specific Heat, Enthalpy and Entropy

Specific heat values for solid cæsium are shown in Table VI.[89]

TABLE VI.- SPECIFIC HEAT OF CAESIUM AT CONSTANT PRESSURE

T, °K.	C_p, g.-cal./g.-mole	T, °K.	C_p, g.-cal./g.-mole
20	4·72	160	6·44
25	5·08	180	6·49
30	5·36	200	6·56
40	5·68	220	6·65
50	5·80	240	6·81
60	5·89	260	7·02
70	5·97	273·15	7·45
80	6·04	280	7·8
100	6·16	290	9·8
120	6·27	310	7·62
140	6·38	320	7·62

An irregularity in the specific heat–temperature curve occurs in a region between 100 and 200°K., within which there is some evidence of hysteresis. As the melting point is approached there is a marked increase in specific heat as with the other alkali metals. If oxygen is present there is a sharp peak in the experimental specific heat curve at about 270°K. resulting from thermal effects associated with the cæsium–oxygen system.

On the basis of much earlier work by Eckhardt and Graefe[90] and by Rengade,[91] Kelley[92] represented the enthalpy or heat content (g.-cal./g.-mole) of solid and liquid cæsium by the equations:

Solid: $H_T - H_{298\cdot16} = 7\cdot24\,T - 2{,}212$ (2% accuracy between 298° and 301·5°K.)
Liquid: $H_T - H_{298\cdot16} = 8\cdot00\,T - 1{,}885$ (2% accuracy between 301·5° and 500°K.)

These correspond to 7·24 g.-cal./g.-mole for the specific heat of the solid and 8·00 g.-cal./g.-mole for the liquid. Thermodynamic functions for solid and liquid cæsium from a compilation by Stull and Sinke[59] in 1956 are shown in Table VII. From low-temperature heat capacity measurements (Table

VI)[89] the enthalpy and entropy of the solid at 298°K. were calculated[59] as 1859 g.-cal./g.-atom and 20·16 g.-cal./g.-atom/degree respectively.

TABLE VII.- THERMODYNAMIC FUNCTIONS FOR SOLID AND LIQUID CAESIUM

Temp., °K.	C_p^o g.-cal./g.-atom/deg.	$H_T^o - H^o_{298{\cdot}15}$ g.-cal./g.-atom	S_T^o g.-cal./g.-atom/deg.	$-(F_T^o - H^o_{298{\cdot}15})/T$ g.-cal./g.-atom/deg.
298	7·50	0	20·16	20·16
300	7·54	14	20·21	20·17
400	7·60	1284	24·09	20·88
500	7·60	2044	25·78	21·70
600	7·60	2804	27·17	22·50
700	7·60	3564	28·34	23·25
800	7·60	4324	29·36	23·96
900	7·60	5084	30·26	24·62

Using his value for the entropy of cæsium vapour (see below) together with a value for the entropy of vaporisation ($\Delta S_{298{\cdot}16} = 22{\cdot}13$ g.-cal./g.-atom/degree) computed from vapour pressure and heat capacity data, Kelley[66,92] estimated 19·8 ± 1·0 g.-cal./g.-atom/degree for the entropy of solid cæsium at 298·16°K. In 1952, 19·8 g.-cal./g.-atom/degree was taken as the U.S. Bureau of Standards[65] selected value at 298·16°K.

From the vibration frequency, Kelley[90] represented the heat content (in g.-cal./g.-mole) of diatomic cæsium vapour by the equation:

$$H_T - H_{298{\cdot}16} = 8{\cdot}94T - 2{,}666 \text{ (1\% accuracy between 298° and 1000°K.),}$$

corresponding to a heat capacity of 8·94 g.-cal./g.-mole.

Recent calculations[60] using spectroscopic data have led to the selection of values for the thermodynamic properties of monatomic and diatomic cæsium vapour shown in Tables VIII and IX.

TABLE VIII.- THERMODYNAMIC PROPERTIES OF MONATOMIC CAESIUM VAPOUR

T, °K.	$-(F^o - H_0^o)/T$ g.-cal./g.-atom/°K.	$(H^o - H_0^o)/T$ g.-cal./g.-atom/°K.	S^o g.-cal./g.-atom/°K.	C_p^o g.-cal./g.-atom/°K.
50	28·1053	4·9680	33·0733	4·9680
100	31·5488	4·9680	36·5168	4·9680
250	36·1009	4·9680	41·0689	4·9680
273·16	36·5411	4·9680	41·5091	4·9680
298·16	36·9761	4·9680	41·9441	4·9680
400	38·4359	4·9680	43·4039	4·9680
500	39·5445	4·9680	44·5125	4·9680
600	40·4502	4·9680	45·4182	4·9680
800	41·8794	4·9680	46·8474	4·9680
1000	42·9880	4·9680	47·9560	4·9681
1200	43·8938	4·9681	48·8619	4·9692
1400	44·6597	4·9685	49·6282	4·9748
1500	45·0024	4·9692	49·9716	4·9813
1600	45·3232	4·9702	50·2934	4·9918
1800	45·9088	4·9746	50·8834	5·0307
2000	46·4333	4·9834	51·4167	5·1026
2200	46·9089	4·9991	51·9080	5·2176
2400	47·3449	5·0239	52·3688	5·3836
2500	47·5503	5·0403	52·5906	5·4874

The entropy of monatomic cæsium vapour at 298·16°K. calculated from

TABLE IX.- THERMODYNAMIC PROPERTIES OF DIATOMIC CAESIUM VAPOUR

T, °K.	$-(F^\circ - H_0^\circ)/T$ g.-cal./g.-mole/°K.	$(H^\circ - H_0^\circ)/T$ g.-cal./g.-mole/°K.	S° g.-cal./g.-mole/°K.	C_p° g.-cal./g.-mole/°K.	$-\Delta Hf^\circ$* kg.-cal./g.-mole	$-\Delta Ff^\circ$* kg.-cal./g.-mole
0	0	0	0	0	10·38	10·38
250	57·467	8·786	66·253	9·081	10·668	6·696
273·16	58·246	8·812	67·058	9·097	10·687	6·327
298·16	59·019	8·836	67·855	9·112	10·708	5·928
400	61·627	8·915	70·542	9·176	10·788	4·282
500	63·623	8·973	72·596	9·236	10·862	2·647
600	65·26	9·02	74·28	9·30	10·93	1·00
800	67·87	9·10	76·97	9·42	11·05	−2·33
1000	69·91	9·18	79·09	9·53	11·14	−5·68
1200	71·59	9·25	80·84	9·65	11·20	−9·06
1400	73·02	9·32	82·34	9·77	11·24	−12·44
1500	73·66	9·35	83·01	9·83	11·26	−14·14

* The reference state in computing the heat and free energy of formation was taken as the monatomic gas.

the Sackur equation (with $R\ln 2$ added to account for the multiplicity in the lowest energy state) is 41·95 ± 0·01 g.-cal./g.-atom/°K.[93] For diatomic caesium vapour, Kelley[93] estimated $\Delta S^0_{298\cdot16} = 66{\cdot}6 \pm 1{\cdot}5$ g.-cal./g.-mole/°K.

Thermal Conductivity

From low temperature thermal conductivity measurements[94] the variation with temperature below 4°K. has been represented by the equation

$$1/\kappa = (1{\cdot}7/T) + 3 \times 10^{-2}T^2$$

where κ is in watt cm.$^{-1}$degree.$^{-1}$

Making use of the Lorentz number, which relates thermal and electrical conductivities, estimates of 0·044 g.-cal.cm.$^{-1}$sec.$^{-1}$degree^{-1} (equivalent to 0·18 watt cm.$^{-1}$degree^{-1})[95] and 0·05 to 0·065 g.-cal.cm.$^{-1}$sec.$^{-1}$degree^{-1} (0·21 to 0·25 watt cm.$^{-1}$degree^{-1})[96] have been made for the thermal conductivity of liquid caesium at its melting point.

Magnetic fields up to 5300 gauss have been shown to be without effect on the thermal conductivity of caesium vapour.[97]

Electrical Resistance

The ratio of the electrical resistance of caesium at low temperatures to that at room temperature or at 0°C. has been studied by a number of workers,[8, 94, 98-103] but no new determinations of specific resistance have been reported. Hackspill's[104, 105] specific resistances of 18·1 μ ohm.cm. at 0°C. and 20·0 μ ohm.cm. at 17°C. for solid caesium and 36·6 μ ohm.cm. at 30°C. and 37·0 μ ohm.cm. at 37°C. for liquid caesium remain the most widely accepted values.

Rather erratic behaviour has been observed in studies of the temperature variation of resistance. On warming a sample of caesium from liquid oxygen temperature to room temperature MacDonald and Mendelssohn[102] obtained the curve of Fig. 3A, showing a discontinuity at about −20°C. which is possibly due to some anomaly in thermal expansion in this region. On recooling to liquid oxygen temperature and again warming to room temperature the curves of Fig. 3B were obtained. Kinks, thought to be due to the presence of other alkali metal impurities, have been observed in the resistance curve in the region of 4 to 10°K.[101-103] Below 3·1°K. the resistance, less the residual resistance, shows a fifth power dependence on temperature.

Measurements of relative resistance over a temperature range covering solid and liquid caesium have led to the following interpolated values:-[8]

T, °K.	−200	−150	−100	−50	0	+50	+100
R/R_0	0·20	0·37	0·55	0·70	1·00	1·87	2·16

There is the usual increase in resistance as the melting point is reached; the resistance of the liquid rises linearly with increase of temperature.

A thin film of caesium, formed by directing a beam of atoms on to a cooled glass surface, will conduct electricity before the number of atoms deposited is sufficient for a monatomic layer.[106-108] At 64°K. conductivity has been detected at a thickness of only 0·35A. or 0·06 atomic layers.[106] Both the resistance and resistivity of the film decrease with increasing thickness, but on stopping deposition the film slowly breaks up and the resistance increases. Figure 3 on page 1518 compares the formation and decay of conductivity for films of caesium, rubidium and potassium deposited at 90°K. with approximately the same beam intensity in each case.[106] Conductivity commenced with caesium at a film thickness of about 1·7 A., and when the film was 20 A. thick its resistance was about 140 times that of the bulk metal. Caesium films are more stable and have a higher conductivity than those of rubidium or potassium

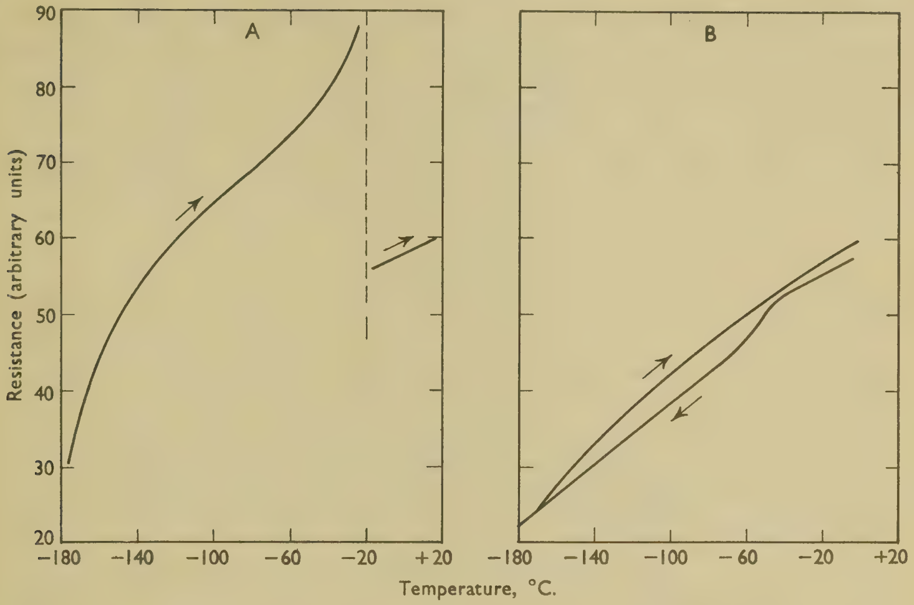

FIG. 3.- VARIATION OF ELECTRICAL RESISTANCE OF CAESIUM BETWEEN LIQUID OXYGEN TEMPERATURE AND ROOM TEMPERATURE

(see also pages 1517, 2163). The rate of decay of conductivity after deposition stops decreases with increasing film thickness and with decreasing temperature. A 5·7 A. thick cæsium film is stable at 64°K. but it decays slowly on raising the temperature to 90°K. In cæsium films approximately 10^4 A. thick the resistivity is only about 4% greater than in the bulk metal.[109] Theoretical treatments of the resistivity of thin cæsium films have been made.[110,111]

Cæsium films, probably monatomic, deposited spontaneously on the walls of glass vessels containing the metal in vacuum are also electrically conducting. The conductivity is greater than for similar films of potassium or rubidium.[112]

Low-temperature measurements of the increase in electrical resistance of cæsium on applying a magnetic field have been made by Justi[100] and by MacDonald.[113]

Values for the relative resistance of cæsium at pressures up to 100,000 kg./cm.^{2} are given in Table X.[114]

The resistance passes through a minimum at 2,500 kg./cm.^{2} and then rises rapidly with increasing pressure. There is a discontinuity in the electrical resistance corresponding to the transition from a body-centred cube to a face-centred cube which occurs in the region of 23,000 kg./cm.^{2} (see page 2295). At higher pressures, where cæsium undergoes an electronic transition in the region of 45,000 kg./cm.^{2} (see page 2295), there is a sharp cusp in the resistance-pressure curve. With increasing pressures the cusp occurs at about 55,000 kg./cm.^{2}, but with decreasing pressures it is lower by almost 20,000 kg./cm.^{2}.

A more detailed study of the resistance variation over a narrower pressure range (0 to 30,000 kg./cm.^{2}) was made earlier by the same author at temperatures of 30° and 75°C.[115] In still earlier work[116] the behaviour at pressures up to 12,000 kg./cm.^{2} was studied at 0°C.

TABLE X.- EFFECT OF PRESSURE ON THE ELECTRICAL RESISTANCE OF CAESIUM

Pressure, kg./cm.^{2}	R/R_0
0	1·0
10,000	1·09 a
20,000	2·12
30,000	4·20 b
40,000	5·96
50,000	8·90
60,000	9·32 c
70,000	7·55
80,000	6·55
90,000	5·88
100,000	5·33

a) Minimum of 0·80 at 2,500 kg./cm.^{2}
b) Transition at 22,000 kg./cm.^{2}; resistances 2·44 and 2·70.
c) Maximum of 11·2 at 54,950 kg./cm.^{2}

Thermoelectric Properties

The thermoelectric power of cæsium relative to platinum was measured by Bidwell[8] between −180° and +200°C. (Fig. 4). A small change of slope at about −80°C. is followed by a marked increase in thermoelectric power as the melting point is approached. The thermoelectric power of the liquid decreases with increasing temperature.

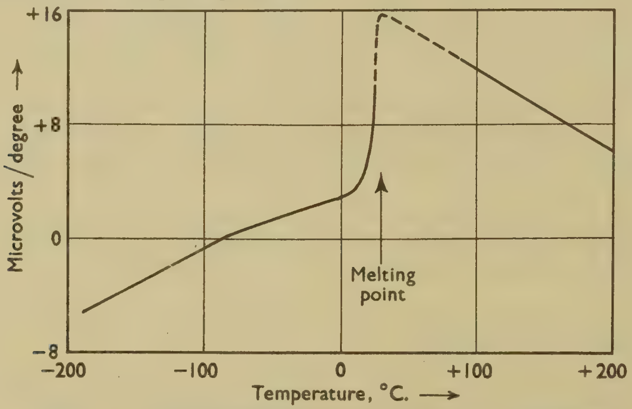

FIG. 4.- THERMOELECTRIC POWER OF CAESIUM

Measurements of the thermoelectric force of cæsium against lead have been made at temperatures between 5° and 65°K.[117] Even at 5°K. the thermoelectric power showed no obvious tendency towards zero.

Magnetic Properties

Several determinations of the mass magnetic susceptibility of cæsium are in close agreement giving room temperature values of $0{\cdot}22 \times 10^{-6}$,[118,119] $0{\cdot}225 \times 10^{-6}$[3] and $0{\cdot}226 \pm 0.001 \times 10^{-6}$.[120] In some earlier studies[121-123] cæsium was, however, reported to be slightly diamagnetic. The susceptibility varies very little with temperature: McLennan *et al.*[118] found the susceptibility at liquid air temperature to be practically the same as at room temperature, whilst Lane[119] obtained $0{\cdot}20 \times 10^{-6}$ for liquid cæsium. McLennan *et al.*[118] reported that their attempts to reproduce the slight increase in susceptibility at the melting point reported by Sucksmith[123] were unsuccessful. For liquid cæsium, Sucksmith[123] found a rise in susceptibility of about $0{\cdot}04 \times 10^{-6}$ between the melting point and 300°C.; all his susceptibility values for cæsium were, however, negative. Böhm and Klemm[3] have given the following figures for atomic susceptibility (mass susceptibility × atomic weight).

Temp. °C.	−183	+20	+100
χ At. $\times 10^6$	34·5	29·9	26·5

Theoretical treatments of the magnetic susceptibility of cæsium have been given.[124,125]

The contribution of the cæsium ion to the diamagnetism of its salts has been evaluated from experimental data on the susceptibility of salts as well as by applying purely theoretical methods. A wide variety of values has resulted. Values for the susceptibility of the cæsium ion in solution derived from measurements on its salts include −45·75,[126] −38·3,[127] −37·3[128,129] and −36·8[130] (all to be multiplied by 10^{-6}), while values for the Cs^+ ion in crystals include $-41{\cdot}0 \times 10^{-6}$[131] and $-35{\cdot}1 \times 10^{-6}$.[132,133] Theoretical treatments have given the following values for free cæsium ions: −55,[134] −43,[135] −39·5,[136] −37·5,[137] −37·21[138] and −33·0[139] (all to be multiplied by 10^{-6}). Klemm[140,141] in a review of the field has given $-33{\cdot}4 \times 10^{-6}$ as the most probable value for the susceptibility of the cæsium ion in solution. For the ion in crystals he gave $-31{\cdot}5 \times 10^{-6}$ when the co-ordination number is 6 and $-31{\cdot}1 \times 10^{-6}$ when it is 8, whilst for the free ion he gave $-34{\cdot}0 \times 10^{-6}$. Another survey[142] recommends $-35{\cdot}0 \times 10^{-6}$ but does not distinguish between the ion in solution and in crystals.[143] There are a number of useful reviews of methods for obtaining ionic susceptibilities and/or of the values resulting from them.[140,142,144-146]

Measurements of the magnetic moment of the ^{133}Cs nucleus have been made by a number of authors;[147-156] the best value has been given as $2{\cdot}5771 \pm 0{\cdot}009$ nuclear magnetons.[157]

As with other metals, the nuclear magnetic resonance frequency of cæsium in its compounds is lower than in the metal itself (Knight shift).[158,42] At room temperature the resonance shift $\Delta H/H$ for ^{133}Cs with respect to an aqueous solution of cæsium chloride is $1{\cdot}49 \times 10^{-2} \pm 0{\cdot}01 \times 10^{-2}$, being greater than for the other alkali metals.[42] The resonance shift decreases with temperature and there is a discontinuous decrease at the melting point, but the total variation over a 200°C. range including the melting point amounts to no more than about 6% of the total shift.[159] Measurements of the magnetic resonance line width and its temperature dependence have also been made.[42] Chemical shifts of the ^{133}Cs magnetic resonance have been found in solid polycrystalline caesium halides.[160]

There has been considerable discussion regarding the spin to be assigned to the ^{133}Cs nucleus.[161-172] The accepted value[157] is 7/2.

Electrode Potentials

The standard electrode potential of cæsium has been measured by Bent, Forbes and Forziati[173] using the indirect method due to Lewis (see Volume II, supplement II, page 404). The two cells employed were:

Cs	CsI in dimethylamine	Cs (0·182% amalgam)
and Cs (0·182% amalgam)	CsOH aq.	Mercuric oxide reference electrode

E.m.f. measurements were made over the range 0–30°C. For solid cæsium the standard electrode potential on the hydrogen scale is −2·923 V. at 25°C. and −2·952 V. at 0°C.; for liquid cæsium at 30°C. it is −2·914 V. These and the values quoted below follow the European convention regarding the sign of the electrode potential. Earlier attempts to apply the method to cæsium were unsuccessful because of the failure to find a solvent for a cæsium salt that would not dissolve the metal.[174] A standard potential of −2·923 V. at 25°C. has also been calculated from thermodynamic data.[175] From measurements of the decomposition voltages of fused cæsium halides, a value of −2·909 V. has been arrived at for the cæsium potential at 18°C.[176] From spectroscopic and thermodynamic data, Gapon[177] has calculated the absolute electrode potential of cæsium to be +0·96 V.

Standard electrode potentials for the five alkali metals in aqueous solution at 25°C. are compared on page 405 in Volume II, Supplement II.

The potential of the ionic double layer has been calculated for cæsium as −0·16 V., from which a value of −2·86 has been obtained for the potential of zero charge (or of the maximum of the electrocapillary curve).[178]

Pleskov has measured electrode potentials of cæsium and other alkali metals in a number of non-aqueous solvents including liquid ammonia,[179] formic acid[180] and acetonitrile.[181] Table XI on page 47 in Volume II, Supplement II is based on some of his results.

Electromotive forces for the cell $Cs|CsCl|Cl_2$, where the cæsium chloride is in the solid or liquid state, have been calculated for temperatures between 25°C. and 1500°C. using thermodynamic data.[182] Similar calculations for other metals permit the construction of an electrochemical series for solid and fused chlorides.[182] The order of the metals varies slightly with temperature.

The cæsium ion was one of those studied by Heyrovsky[183,184] in his first polarographic investigations: he found its deposition potential at a dropping mercury cathode in aqueous solution to be −1·837 V. relative to a normal calomel electrode. Cæsium ions may be discharged at a mercury cathode in neutral and alkaline solutions without the accompaniment of hydrogen evolution because of compound formation between cæsium and mercury and the high hydrogen over-voltage at mercury. Choice of supporting electrolyte is, however, limited on account of the very negative potential, tetra-alkylammonium halides or hydroxides being virtually the only usable compounds.[185] With tetramethylammonium chloride or hydroxide as supporting electrolyte Heyrovsky has given values of −2·13 V.[186] and −2·09 V.[187] for the half-wave potential of cæsium ions in aqueous solution relative to a normal calomel electrode. More recent studies have given the half-wave potential in 0·1 M.-tetramethylammonium hydroxide at 25°C. as −2·135 V. against a normal calomel electrode.[188,189] Alcohol–water mixtures are frequently used in obtaining polarograms of the alkali metals since they give better developed waves than do purely aqueous media. In 50% ethyl alcohol, with 0·1 M.-tetraethylammonium hydroxide as supporting electrolyte, the half-wave potential of cæsium is −2·05 V. relative to a saturated calomel electrode.[186] It is so close to those of rubidium, potassium and sodium that these four metals cannot be differentiated polarographically.[185]

At −36°C. in liquid ammonia saturated with tetrabutylammonium iodide as supporting electrolyte, the half-wave potential of the cæsium ion relative to a 0·1 N.-$Pb/Pb(NO_3)_2$ reference electrode is −1·15 V.[190]

Ionization Potentials and Electronegativity

Ionization potentials for cæsium, in electron volts, obtained by calculation from spectral series limits or by extrapolation along the isoelectronic sequences are as follows:[191]

I	II	III	IV	V	VI	VII	VIII	IX	X
3·89	23·4	(34)	(46)	(62)	(74)	(86)	(117)	(132)	(246)

Bracketed values have been obtained by the latter method.

Ionization of cæsium can result in various ways, for example, by electron impact[192] or by the action of ultra-violet light (see page 2314) or other ionizing radiations.[193,194] Caesium atoms may also be ionized on hot surfaces of metals such as tungsten or platinum since the work function of these surfaces is greater than the ionization potential of cæsium[49–52,195–198] (see pages 2298 and 2300).

Cæsium has a value of 0·7 on Pauling's electronegativity scale, values for the other alkali metals being Li, 1·0; Na, 0·9; K, 0·8; Rb, 0·8.[13]

Optical Properties

As with the other alkali metals, thin films of cæsium that are quite opaque to visible light become transparent in the near ultra-violet region of the spectrum.[199,200] Transmission starts to become appreciable with cæsium at about 4400 A., a longer wave-length than for any other alkali metal.[199]

Reflection of monochromatic plane polarised light from free surfaces of caesium has been studied by Ives and Briggs[200] who from their measurements calculated the values of Table XI for the refractive index (*n*), the extinction coefficient (K_0), the reflecting power for normal incidence (*R*), the principal angle of incidence ($\bar{\phi}$) and the principal azimuth ($\bar{\psi}$).

TABLE XI.- OPTICAL CONSTANTS OF CAESIUM

λ, (A.)	n	K_0	R (%)	$\bar{\phi}$	$\bar{\psi}$
5780	0·264	1·123	63·1	58° 54′	49° 17′
5461	0·278	0·950	56·1	56° 39′	49° 47′
4358	0·425	0·438	23·5	47° 53′	53° 24′
4047	0·540	0·320	12·7	44° 4′	57° 25′
3650	0·671	0·233	5·72	40° 41′	66° 9′
3126	0·827	0·174	1·79	41° 49′	76° 29′
2536	0·916	0·143	0·74	43° 36′	80° 39′

Figure 5 shows optical transmission curves, calculated from the above data, for cæsium films with thicknesses of $1{\cdot}25 \times 10^{-5}$, $2{\cdot}5 \times 10^{-5}$ and $5{\cdot}0 \times 10^{-5}$ cm.

Earlier measurements of the optical properties of cæsium were made by Nathanson.[201–204] Using light of 4550A. to 6800A. he obtained values mostly between 0·30–0·35 for the refractive index. He also showed that the optical properties of liquid cæsium (at 33°C.) were practically identical with those of the solid (at 23°C.).[203,204]

The optical absorption of multiatomic layers of cæsium adsorbed on calcium fluoride (page 2301) is similar to that of thin films of solid cæsium, there being a rapid decrease in absorption on passing from the visible to the ultra-violet region of the spectrum.[205] For thinner (monatomic) layers the visible absorption is very small and there is a gradual rise in absorption towards ultra-violet wave-lengths.

There have been a number of theoretical considerations of the optical properties of cæsium and the other alkali metals;[206–213] particular attention has been directed to the explanation of their transparency in the ultra-violet.

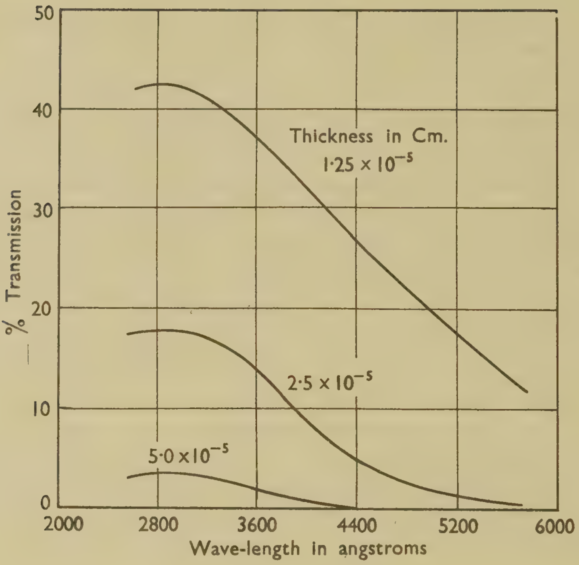

FIG. 5.- OPTICAL TRANSMISSION OF CAESIUM FILMS

Studies of anomalous dispersion in caesium vapour have been made in the region of the first two doublets of the principal series.[214-219] Magnetic double refraction (the Voigt effect) has also been studied in caesium vapour.[220]

Photoelectric Properties

The photoelectric properties of caesium, like those of the other alkali metals, depend on the state of the surface and the film thickness, and are very sensitive to the presence of impurities including even slight traces of many gases. It therefore becomes difficult to isolate the properties characteristic of the pure metal, and many of the effects observed with supposedly pure caesium probably owe their existence to the presence of adsorbed gases. Several books on photoelectricity have paid considerable attention to the photoelectric properties of caesium and the other alkali metals.[81,221-223]

Thick films of gas-free caesium at −180°C. have been reported by Brady[224] to have a photoelectric threshold of 6300A. which corresponds to a work function of 1·96 e.v. Mayer[225] gave the work function of thick layers of gas-free caesium as 1·94 e.V. Theoretical treatments have given values of 2·15[226] and 2·05 e.V.[227] for the work function of caesium.

As a film of caesium is deposited by means of an atomic beam on a gas-free silver surface, the initial effect is that the threshold of the substrate moves to longer wave-lengths. Brady[224] found that the threshold reached an extreme position of 6600A. at a film thickness of 1·5 atomic layers and that with further increase of thickness the threshold wave-length returned to the value (6300A.) for the bulk metal. The photoelectric emission increased with film thickness up to five atomic layers before falling to that for bulk caesium. There was no further change in the photoelectric properties beyond a thickness of ten atomic layers.[224] Brady's thickness estimates have been considered too high because of the neglected roughness of the substrate.[228] Ives and Olpin[229] obtained an extreme threshold of 8950A. for caesium films on silver. This is very close to the wave-length of the first line of the principal series of cæsium (8943 A.), and the same correlation was found for the other alkali metals. It has, however, been suggested[230] that the substrates probably contained oxygen which is known to cause large threshold shifts. From later work[231] it appears that for surfaces completely free from contamination there would be no variation of photoelectric sensitivity with film thickness.

For compact layers of cæsium, Kluge[232] reported four small selective maxima at 2400, 2850, 3600 and 5000 A., which were attributed to selective optical absorption bands of adsorbed cæsium atoms. The photoelectric efficiency was ~10^{-4} coulombs per calorie at the three shorter wave-length maxima and ~$0{\cdot}3 \times 10^{-4}$ coulombs per calorie at 5000 A. Admitting hydrogen to a pressure of ~0·3 to 0·4 mm. Hg approximately doubled the efficiency at the shorter wave-lengths and more than doubled it at 5000 A.

Composite Photocathodes.

Many varieties of photocathode have been described in which cæsium atoms are separated by a dielectric (usually Cs_2O) from a metal substrate. Caesium itself does not make a satisfactory substrate at room temperature because of its high mobility: a thick layer of cæsium forms on the Cs_2O and the surface has low sensitivity.[233] At −180°C., where the mobility is lower, only a monatomic layer of caesium forms and the surface has a high sensitivity. It is usual to employ a substrate of silver, tungsten, or some other metal, and the properties to the final cæsium–oxygen photocathode are very dependent on the exact method of preparation.

If, at room temperature, oxygen is adsorbed on silver, the excess pumped off and cæsium admitted, a monomolecular layer of cæsium oxide is formed between the substrate and the excess cæsium. Such a photocathode has a threshold at ~9000 A. and a maximum response at ~6100 A.[234] A surface with a thicker caesium oxide interlayer (formed by depositing cæsium on silver, oxidising the caesium, and finally admitting more cæsium) also has a maximum response at ~6100 A. but its threshold is shifted to ~11000 A.[234] By heating a clean silver surface in oxygen at 360°C., cooling it, pumping off the excess oxygen, and then heating at 300°C. in cæsium vapour a photocathode is produced which has no maximum in the visible region of the spectrum but whose photoelectric emission increases steadily from a threshold at ~8000 A. to a maximum at 3500 A.[233] In this case oxygen ions and cæsium ions and atoms are considered to be adsorbed side by side on the surface of the silver,[235] and in the notation of de Boer[81] the structure of the photocathode may be represented [Ag]–O, Cs.

In a second class of composite oxide cathodes a thick layer of silver oxide is first formed on a silver surface, excess of cæsium is admitted and the surface heated to between 200 and 250°C. whereupon the silver oxide is reduced and there is formed a thick layer of caesium oxide throughout which particles of silver are dispersed.[233] Some of the excess cæsium becomes adsorbed on the surface and in de Boer's notation the photocathode can be represented [Ag]–Cs_2O, Ag–Cs. A glow discharge in oxygen has frequently been used to produce the Ag_2O layer, the surface to be oxidised being made the cathode.[236–241] Koller[233] who first made [Ag]–Cs_2O, Ag–Cs surfaces found two maxima at 7500 A. and 3500 A. Kluge[240] for such surfaces reported a threshold at ~12,000 A. and maxima at ~7500 A. and ~4,200 A., but in a more detailed examination[242] he found two maxima at 3700 A. and 2900 A. in place of the one at ~4200 A. Fleisher and Görlich[243] found maxima at 3750 A. and 2800 A. in addition to that at 7500 A., the sensitivities at the maxima being ~22×10^{-3}, ~$7{\cdot}5 \times 10^{-3}$ and 25×10^{-3} coulombs per calorie respectively.

The sensitivities of photocathodes of the above type may be increased by introducing additional metal atoms, especially silver and gold, into the caesium oxide layer. This may be done by subliming the metal onto the [Ag]–Cs_2O, Ag–Cs surface after its formation,[243–246] or the metal may be introduced into the silver oxide layer before reduction with caesium.[247] In the latter case the metal may be evaporated on to the silver oxide or – where the added metal is to be silver – a thick layer of silver oxide may be partially reduced with hydrogen.[247] Asao,[245] for a cathode containing a 5% excess of caesium over that required to reduce the silver oxide (originally 70 molecules thick), found a sensitivity of 7 to 10μ amp./lumen for a light source of colour temperature 2700°K., but when silver atoms to about two-thirds the number of Cs_2O molecules were evaporated on to the surface and the cathode heat treated the sensitivity increased to ~50μ amp./lumen. Cathodes with thicknesses two to three times as great as these had their sensitivity increased from 20–30μ amp./lumen up to ~95μ amp./lumen by this technique.[245] Sewig[246] introduced many other metals into [Ag]–Cs_2O, Ag–Cs cathodes, and all those studied (Cu, Au, Ta, Mo, W, Fe, Ni, Pt) were found to result in an increased sensitivity towards white light, tantalum, tungsten and nickel being particularly effective. Introduction of excess of caesium atoms into the caesium oxide layer can also give rise to an increased sensitivity. This may be done by prolonged heating in caesium vapour[239] or by exposure to a caesium ion beam.[248] Such treatments give rise to surfaces that may be represented: [Ag]–Cs_2O, Cs, Ag–Cs. Fig. 6 shows the spectral response for a surface of this type.[20]

Hartmann[249] has reviewed the production of [Ag]–Cs_2O, Ag–Cs photocathodes.

Photocathodes may also be produced with interlayers containing sulphur, selenium or tellurium instead of oxygen. The following table summarises their main characteristics.[250]

	Cs–O	Cs–S	Cs–Se	Cs–Te
Threshold, A. Units	10,000–12,000	8,500–10,000	7,500–8,500	7,100
Wave-length of maximum response, A. Units	7,000–8,000	4,750–5,300	4750	4,500
Sensitivity, μ amp./lumen (colour temp., 2360°K.)	30–50	10–20	5–10	5–10

Caesium hydride[232] and naphthalene[251] dielectric layers have also been studied.

Caesium deposited on a thin layer of calcium or barium fluorides on a silver substrate is photosensitive.[234] In both cases the sensitivity at first increases linearly with the amount of caesium deposited but then, after passing through a maximum, it decreases to a value which is independent of further deposition. On calcium fluoride the maximum sensitivity is ~0·7μ amp./lumen and the final value ~0·5μ amp./lumen, whilst on barium fluoride the maximum and final values are ~1·8 and ~0·9μ amp./lumen respectively. At the thicknesses corresponding to maximum sensitivity the thresholds are 7000 A. on CaF_2 and 7,300 A. on BaF_2.[234]

Fatigue.

On continued exposure to strong illumination, composite layer caesium photocathodes exhibit fatigue. The threshold wave-length and the wave-length of maximum response become shorter, and the sensitivity at the maximum also decreases. These effects are due to (*a*) an increase in the number of temporarily unneutralised positive caesium ions on the surface and in the interlayer, as a result of which there is an increased energy requirement for ionisation of the remaining adsorbed atoms, and (*b*) a decrease in the number of free caesium atoms on the surface because of migration of caesium ions from the surface into the interior of the cathode under the influence of the applied field.[239,252,253] Fig. 6 shows the spectral response for a fresh [Ag]–Cs_2O, Cs, Ag–Cs photocathode and for one where fatigue has set in after prolonged exposure to white light.[239]

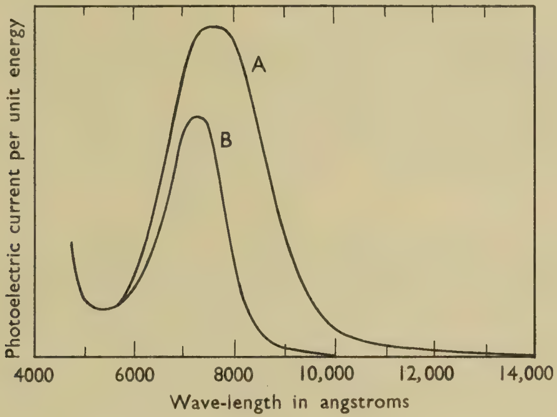

FIG. 6.- SPECTRAL RESPONSE OF AN [Ag]–Cs_2O, Cs, Ag–Cs PHOTOCATHODE A) IN A FRESH STATE B) AFTER PROLONGED EXPOSURE TO LIGHT

The rate of fatigue on exposure to light decreases with increasing wave-length and with infra-red light no decrease in sensitivity occurs; in fact, exposure to infra-red light speeds the recovery of fatigued cells.[239,254,255] Fatigued photocells may also have their sensitivity restored by keeping in the dark or by heating for a short time at about 200°C.[239,254] The presence of a large number of excess caesium and silver atoms in the caesium oxide layer reduces the susceptibility to fatigue.[256]

'Alloy' Photocathodes.

Photocathodes of very high sensitivity can be produced by evaporating a thin layer of a metal such as bismuth, antimony, lead or thallium on to glass or quartz and exposing the layer to caesium.[257] These surfaces, which were first prepared by Görlich,[257] have the virtue of being semi-transparent. A bismuth–caesium photocathode formed in this way shows a maximum response at ~4300 A. and the response extends to about 7000 A.[257,258] Exposure to oxygen at a low pressure can shift the maximum to longer wave-lengths. Several measurements[257–262] of the wave-length of maximum response for antimony–caesium photocathodes have given values of 4200–4600 A.; other studies[263–265] have given values about 3500 A. and have shown the response to extend in the ultra-violet to about 1500 A. Spectral sensitivity measurements have also been made at low temperatures.[266] For Sb–Cs cathodes, Luk'yanov[260] found a yield of 0·3 electron per quantum and a sensitivity of 40–50 μ amps. per lumen for light having a colour temperature of 2350°K. Using light with a colour temperature of 2870°K., Khlebnikov[267] obtained sensitivities of 60 to 100 μ amps. per lumen for Sb–Cs cathodes and found them to show little sign of fatigue. Other work has given the integral sensitivities of Sb–Cs, As–Cs and Bi–Cs cathodes as 70, 40, and 15 μ amps. per lumen respectively.[268] The sensitivity of Ga–Cs, In–Cs and Tl–Cs cathodes is approximately 1 μ amp./ per lumen.[269]

The work of Sommer[261] and of others[270–274] has shown that the active substances in these photosurfaces are intermetallic compounds rather than alloys. For antimony–caesium cathodes the intermetallic compound is $SbCs_3$. This is a semiconductor, its specific resistance being about 1 ohm cm., a value approximately 10^5 times that for metals and normal alloys. Sommer[261] tried all the metals of the fourth and fifth Groups of the periodic table in combination with caesium and found that no other alloy had a photoelectric sensitivity as high as that of $SbCs_3$.

These semitransparent cathodes may be deposited on the surface of thick cæsium oxide photocathodes to give a combined response which is comparatively uniform throughout the visible region of the spectrum.[275,276]

Use is made of silver–cæsium oxide–cæsium surfaces and cæsium alloy surfaces (in particular Sb–Cs) in commercial phototubes. The preparation and characteristics of a number of these are described by Zworykin and Ramberg.[277]

Photoionization.

Photoionization of cæsium vapour has been studied by a number of workers using a variety of methods.[193,278-287] The ionization per unit light intensity is at a maximum at the wave-length of the principal spectral series (3184 A.) but ionization can occur at longer as well as shorter wave-lengths.[193,278,282,283] That at longer wave-lengths shows small maxima at the absorption lines of cæsium and is attributed to atoms in highly excited states being ionised by collision.[283] On the short wave-length side of the series limit, both the ionization efficiency and the light absorption fall to a minimum at about 2800 A. and then increase with further decrease of wave-length.[193,279,284-287] Presence of foreign gases has been observed to decrease the light absorption.[287,288]

At the series limit, values of $2{\cdot}2 \pm 0{\cdot}1 \times 10^{-19}$,[287] $2{\cdot}3 \pm 0{\cdot}2 \times 10^{-19}$ [280,281] and 6×10^{-19} cm.^{2} [284] have been obtained for the atomic absorption cross section.

Theoretical treatments of photoionization of the alkali metals give a reasonable measure of agreement with experiment.[289,290]

Miscellaneous Physical Properties

Ultrasonic waves of frequency 12 Mc./sec. have a velocity of 967 ± 10 m./sec. in liquid cæsium at its melting point.[33] Between the melting point and 130°C. the temperature coefficient is $-0{\cdot}3$ m.sec.$^{-1}$degree^{-1}.

By the use of the Stokes–Einstein equation the coefficient of diffusion of caesium in mercury at 8–15°C. has been calculated[291] from atomic radius and viscosity data to be 0·41 cm.^{2} per 24 hr., in reasonable agreement with the earlier experimental value of 0·45 cm.^{2} per 24 hr. at 7·3°C. (Mellor, II, 456).

An experimental determination[292] of the Hall constant of cæsium has given −0·0078, while theoretically calculated values are −0·0073[293] and −0·007375.[294]

The mean free path of caesium atoms has been measured in a number of gases including hydrogen, nitrogen, rare gases, and cæsium vapour.[295,296]

Pure caesium compounds are not radioactive[297,298] although commercial preparations may contain impurities which impart a feeble radioactivity.[299,300]

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PROPERTIES OF THE CAESIUM ION

Some properties of the cæsium ion, and some properties that relate to both the metal and its ion, have been dealt with under the appropriate sections above. Other properties of the Cs^+ ion will be considered here.

The Ion in Solution.

The heat and free energy of formation of the aqueous cæsium ion at 25 °C. are −59·2 and −67·41 kg.-cal. g.-ion^{-1} respectively.[1] On the assumption of equal heat capacities for Cs^+ and I^- ions a value of −15·9 g.-cal. g.-ion^{-1}degree^{-1} has been obtained for the heat capacity of the cæsium ion at infinite dilution.[2] From thermal data for the reaction:

$$CsClO_4\text{ (solid)} \rightarrow Cs^+\text{ (aq.)} + ClO_4^-\text{ (aq.)},$$

Latimer *et al.*[3] computed a value of 31·8 ± 0·6 g.-cal. g.-ion^{-1}degree^{-1} for the entropy of the cæsium ion (relative to that of the hydrogen ion) in aqueous solution at 25°C. The U.S. Bureau of Standards selected value[1] for the entropy of the aqueous cæsium ion at 25 °C. is also 31·8 g.-cal. g.-ion^{-1}degree^{-1}.

After employing a variety of methods to calculate the effective diameter of the hydrated cæsium ion, Kielland[4] took a rounded value of $2{\cdot}5 \times 10^{-8}$ cm. for this dimension and then used the Debye–Hückel theory to compute the activity coefficients for the cæsium ion in aqueous solution at 25°C. that are shown in Table XII.

TABLE XII.- ACTIVITY COEFFICIENTS OF THE Cs^+ ION IN AQUEOUS SOLUTION AT 25°C.

Total Ionic Concentration	0·001	0·002	0·005	0·01	0·02	0·05	0·1	0·2
Activity Coefficient	0·975	0·964	0·945	0·924	0·898	0·85	0·80	0·75

A value of zero is obtained for the hydration number of the Cs^+ ion from the partial molar volume[5] – a method that is considered to give a measure of the primary hydration (see Volume II, Supplement II, page 56). Higher values result from transference, dialysis and other methods.[6,7]

Values calculated for the heat of hydration of the Cs^+ ion have included 61,[8] 62·0,[9] 63,[10] 79[11] and 80[12] kg.-cal./g.-ion, while the free energy of hydration has been calculated as 59,[8] 60·8,[9] and 71·5[12] kg.-cal./g.-ion. The entropy of hydration has been given as 4[9] and as 7·0[8] g.-cal./degree/mole.

In Table XIII are shown values for the equivalent conductivity or mobility of the cæsium ion at infinite dilution in water taken from a compilation[13] which makes use of conductivity and transport data from several sources.

The values at 0° and 18°C. are said to be reliable only within several units; those at 5°, 15°, 25°, 35°, 45° and 55°C. are reliable to within the first

TABLE XIII.- MOBILITY OF THE Cs^+ ION AT INFINITE DILUTION IN WATER

Temp., °C.	0	5	15	18	25	35	45	55
λ_∞	44	$50{\cdot}0_3$	$63{\cdot}1_6$	67	$77{\cdot}2_6$	$92{\cdot}1_0$	$107{\cdot}5_3$	$123{\cdot}6_6$

decimal place. Mobilities of the cæsium ion in a number of non-aqueous solvents have been estimated from conductivity data for cæsium salts.[14,15]

Diffusion coefficients at infinite dilution may be obtained from the above mobility data using Nernst's limiting formula $D^0 = RT\lambda_\infty/zF^2$. At 25°C. it leads to $2{\cdot}06 \times 10^5$ cm.^{2}sec.$^{-1}$ for the self diffusion coefficient of the cæsium ion at infinite dilution in water. An open-ended capillary tube method, making use of ^{134}Cs as radiotracer, has given the values of Tables XIV and XV for the self-diffusion coefficient of the cæsium ion in aqueous solutions of cæsium iodide and cæsium chloride at 25°C.[16]

TABLE XIV.- SELF-DIFFUSION COEFFICIENTS OF Cs^+ IN CsI (AQ.) AT 25°C.

Cs^+ Concentration, g.-ion/litre	$D \times 10^5$, cm.^{2}/sec.
0·00141	2·091 ± 0·020
0·04765	2·058 ± 0·015
0·1136	2·047 ± 0·011
0·5126	2·076 ± 0·037
0·6900	2·007 ± 0·001
1·195	2·094 ± 0·025

TABLE XV.- SELF-DIFFUSION COEFFICIENTS OF Cs^+ IN CsCl (AQ.) AT 25°C.

Cs^+ Concentration, g.-ion/litre	$D \times 10^5$, cm.^{2}/sec.
0·050	2·055 ± 0·020
0·100	2·040 ± 0·010
0·250	2·012 ± 0·070
0·500	1·990 ± 0·010
1·000	1·988 ± 0·010
2·250	1·964 ± 0·013
3·700	1·841 ± 0·010

The specific viscosity of the cæsium ion in 0·1 N. aqueous solution has been calculated as −0·0075.[17]

From the work of Okazaki on the Faraday effect of salts in aqueous solution the following values of the magnetorotatory power of the Cs^+ ion (in min. cm.^{2} gauss^{-1}g.-ion^{-1}) have been derived on the basis of a zero value for the hydrogen ion:[18]

Wave-length, A.	5900	5500	5100	4700	4300	3900	3500
$[M]$	0·70	0·74	0·86	1·05	1·35	1·70	1·95

Okazaki's molecular magnetorotation constant, Φ, (see Volume II, Supplement II, page 422) has a value of $3{\cdot}35 \times 10^{-14}$ for the cæsium ion.[19]

The refractivity of the cæsium ion in aqueous solution for the sodium D-line is 6·24.[20]

Exchange between Cs^+ ions and other ions has been studied with synthetic cationic exchange resins[21-29] as well as with natural exchangers such as clays and minerals.[30-39] For ions of equal charge the strength of binding of an ion by an exchanger increases with decreasing hydrated radius, and in dilute solutions the adsorption or exchange affinities of alkali metal ions follow the series $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$.[21,24,30]

Refs. p. 2323

The Gaseous Ion.

Cæsium ions are readily produced by heating a cæsium compound, usually mixed with other substances, on a metal filament.[40-52] The ions can then be accelerated to the required potential in an electric field. A widely used ion source[44-48] is that introduced by Kunsman[40-43] comprising a mixture of iron oxide with about 1% of a cæsium compound and, in some cases, with about 1% of aluminium oxide. The velocity and saturation current of cæsium ions emitted from a Kunsman anode have been studied by Gille[47] at anode temperatures from 650° to 1300°C. Cæsium aluminosilicate glasses, prepared for example by heating a mixture of aluminium nitrate, cæsium carbonate and powdered quartz in a carbon crucible, have been used by a number of workers.[49-51] A tungsten filament heated to a temperature above 1200°K. in cæsium vapour has been used by other workers as a source of cæsium ions[54-59] (see pages 2298 and 2300). Caesium ions can also be produced by photoionization and by the action of charged particles (see pages 2314 and 2309).

The heat of formation of the gaseous cæsium ion is 110·081 kg.-cal. g.-ion^{-1} at 298·16°K.[1]

The mobility of the Cs^+ ion (in cm./sec./volt/cm.) in various gases at one atmosphere and 20°C. is as follows[44,60]

Helium	19·2	Xenon	0·99
Neon	6·49	Hydrogen	13·4
Argon	2·23	Nitrogen	2·25
Krypton	1·44		

Other measurements in the rare gases are in close agreement with these figures.[50] The temperature variation of the mobility has been studied in helium between 79° and 492°K.,[61] and in xenon between 195° and 450°K.[51] In helium, the mobility of Cs^+ ions at constant density passes through a maximum at about 215°K., while in xenon it is practically constant within the temperature range studied. Mobility measurements have also been made in helium–xenon mixtures.[62] Alkali metal ions, in the presence of water vapour, acquire a cluster of water molecules which reduces their mobility. The effect of small concentrations of water vapour has been studied for the Cs^+ ion in helium, neon, argon, and krypton,[50] and other measurements have been made in water vapour alone.[63] The mobility of Cs^+ ions in a bunsen flame has also been measured.[64]

Ionization of the inert gas by cæsium and other alkali metal ions has been the subject of several investigations.[65-72,45,48] Beeck and Mouzon[66-70] found that, in general, an inert gas was most easily ionized by the ion of the alkali metal with an atomic number closest to its own. Their values for the potentials (ion velocities) required by the Cs^+ ion to ionize neon, argon, krypton and xenon were 437 V., 365 V., 143 V. and 105 V. respectively.[68,70] Later measurements using a space charge method sensitive to any resulting positive ions but unaffected by secondary electrons, which it has been suggested may have caused interference in the measurements of Beeck and Mouzan, have given argon, 338 V.; krypton, 200 V.; and xenon, 77 V.[48]

Optical excitation by cæsium ions has been studied in the rare gases[52,73] and in mercury vapour.[74]

Studies have also been made of the reflection of ions and the emission of secondary electrons on bombarding a number of metal surfaces with cæsium ions.[53,75-78]

The ionic refractivity of the gaseous cæsium ion for the sodium *D*-line is 6·24.[20] Values for the polarisability of the cæsium ion include 2·35 × 10^{-24},[79] 2·45 × 10^{-24},[80] 2·577 × 10^{-24} [20] and 2·79 × 10^{-24}.[81] Other dielectric parameters of the cæsium ion have been evaluated.[82-84]

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SOLUTIONS OF CÆSIUM

Cæsium dissolves readily in liquid ammonia to give deeply coloured solutions. The stability of solutions of the alkali metals in liquid ammonia decreases with increasing atomic weight, those of cæsium deteriorating quite rapidly with formation of amide:[1-3]

$$Cs + NH_3 \rightarrow CsNH_2 + \tfrac{1}{2}H_2$$

Presence of impurities can greatly increase the rate of decomposition (see Volume II, Supplement II, page 427). Whereas it has been reported[1] that at room temperature a half-saturated solution of cæsium in ammonia is completely decomposed in 1 to 2 hr., other workers[4] have prepared, in quartz, very dilute solutions of caesium in ammonia that could be kept for several days without decoloration.

The rate of solution of the alkali metals in liquid ammonia increases from lithium to cæsium.[5] A zero heat of solution has been found for cæsium in ammonia.[6]

On freezing cæsium–ammonia solutions a deep bronze-coloured solid eutectic is formed; the eutectic temperature is −118°C.[7] Cæsium adsorbed on films of solid ammonia at −183°C. and a pressure of 10^{-3} to 10^{-4} mm. of mercury is reported to show the same optical absorption as in solution.[8] The absorption starts at 5600 A. and increases towards longer wave-lengths.

Measurements at −33° and −53°C. of the magnetic susceptibility of caesium dissolved in liquid ammonia are shown in Table XVI.[9]

Solution of cæsium has been reported in methylamine,[10,11] ethylamine[12] and ethylenediamine.[13] It is insoluble in dimethylamine.[14]

There is complete miscibility of cæsium metal with its halides at and

Refs. p. 2325

TABLE XVI.- ATOMIC SUSCEPTIBILITY OF CAESIUM IN AMMONIA

At −33°C.		At −53°C.	
g.-atom Cs/litre	$\chi_A \times 10^6$	g.-atom Cs/litre	$\chi_A \times 10^6$
0·00415	1130	0·00432	755
0·00582	1245	0·00605	1020
0·00690	1013	0·00718	657

above the melting points of the pure halides.[15] An unbroken 'S'-shaped liquidus curve connects the melting point of the salt with the eutectic point which is practically coincident with the melting point of the metal. In the case of caesium fluoride, for example, the solubility in the metal at 30°C. is less than 0·001 mole%. Fig. 7 shows the major portion of the phase diagrams for the systems Cs–CsF, Cs–CsCl and Cs–CsI.

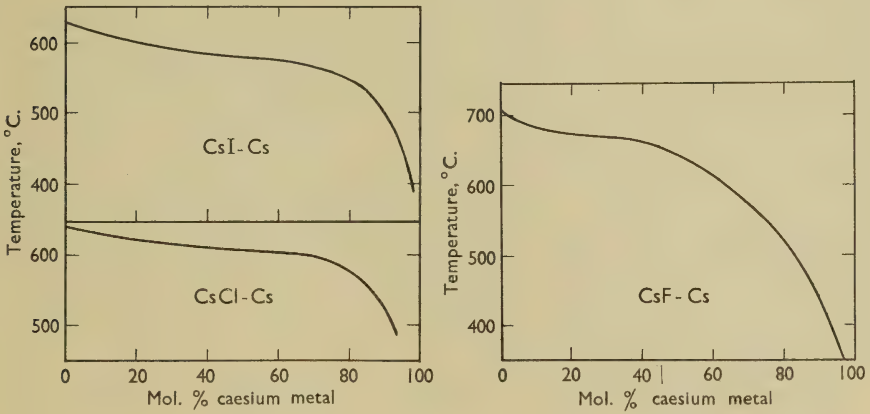

FIG. 7.- THE SYSTEMS CAESIUM IODIDE–CAESIUM, CÆSIUM CHLORIDE–CÆSIUM AND CAESIUM FLUORIDE–CAESIUM

Although on cooling solutions of cæsium in its halides the solid salt that separates is essentially pure salt, it contains a small amount of cæsium metal which gives it a deep purple-blue-black colour.

The heats of solution of cæsium fluoride, chloride and iodide in metallic caesium have been given as 10 ± 0·5, 22 ± 2, and 18 ± 1 kg.-cal./g.-mole respectively.[15]

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ATOMIC WEIGHT AND ISOTOPES

Up to 1934 the internationally accepted value for the atomic weight of cæsium was 132·81, a value based primarily on analyses of cæsium chloride, bromide and nitrate carried out by Richards and Archibald[1] in 1903. The simple isotopic nature of cæsium as revealed by Aston in 1921 (see below) suggested an atomic weight approximating more closely to the mass number of 133, but a further comparison against silver carried out in 1928 using cæsium chloride purified by recrystallisation of cæsium alums substantiated the value of 132·81.[2] In 1933, Baxter and Thomas[3,4] made further determinations of the atomic weight using cæsium chloride that had been subjectedto a much longer purification process. The cæsium salt was recrystallised numerous times as the nitrate, the perchlorate, and the dichloroiodide before being further recrystallised as the chloride. Spectroscopic analysis showed the cæsium chloride to be free from potassium and rubidium. The chloride was prepared for weighing by fusion in a platinum boat and was compared with silver nephelometrically. The resulting atomic weight was 132·91 in agreement with the value obtained by Aston[5,6] from mass spectrograph measurements. Use of nitrogen, hydrogen andhydrogen chloride atmospheres during the fusion process all gave similar values. The only explanation of the lower values obtained by the earlier workers has been that the material they used may not have been completely free from potassium and rubidium. Further determinations of the atomic weight by Baxter and Harrington[7] in 1940 using essentially the same procedure gave a value of 132·913.

The value accepted by the International Commission on Atomic Weights (1955)[8] remains 132·91 adopted in 1934.[9]

Caesium has only one naturally occurring isotope, namely that with a mass number of 133.[10–13] Mass spectrometric investigation has set the upper limits for the natural abundance of other isotopes relative to ^{133}Cs as follows:[13]

^{137}Cs	1/100,000
^{136}Cs	1/100,000
^{135}Cs	1/50,000
^{134}Cs	1/6,000
^{132}Cs	1/4,000
^{131}Cs	1/20,000
^{130}Cs	1/100,000

A number of cæsium isotopes with short half-lives have been produced artificially by nuclear reactions. A review, which also summarises methods of production and disintegration schemes, lists the following:[14]

Isotope	Approx. Half-Life	Isotope	Approx. Half-Life
^{125}Cs	45 min.	^{136}Cs	14days
^{127}Cs	5·5 hr.	^{137}Cs	33years
^{128}Cs	3 min.	^{138}Cs	33min.
^{129}Cs	31 hr.	^{139}Cs	9min.
^{130}Cs	30 min.	^{140}Cs	66sec.

continued on following page

Isotope	Approx. Half-Life	Isotope	Approx. Half-Life
^{131}Cs	10 days	^{141}Cs	short
^{132}Cs	7 days	^{142}Cs	1 min.
^{134}Cs	2 years	^{143}Cs	short
^{135}Cs	3×10^6 years	^{144}Cs	short

From the plot of mass defect against mass number constructed using the accurately known masses of other elements the mass of ^{133}Cs has been estimated[15] as 132·948 ± 0·003.

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SECTION LXXXIII

THE CHEMICAL REACTIONS AND ALLOYS OF CAESIUM

By Mrs. F. DICKINSON

CHEMICAL REACTIONS

Caesium is difficult to handle because it burns in air as soon as it is removed from an inert covering oil. Reaction with dry oxygen occurs at very low temperatures and pressures.[1] At −80°C. reaction appears to begin with cæsium after a few minutes; at −40°C. the metal rapidly darkens but the reaction is not accompanied by luminescence. An old statement that cæsium is scarcely attacked by dry oxygen at ordinary temperatures may perhaps be accounted for by the fact that oxidation is arrested by traces of impurity on the metal surface. Oxidation is, however, promoted by traces of moisture.[2] Caesium amalgam oxidises instantaneously in air or dry oxygen and the reaction is complete in 4–7 days. The black mass formed gives a vigorous evolution of gas on treatment with water leaving a green powder of mercurous oxide, Hg_2O. The amount of oxygen given off corresponds to a composition of $Cs_2O_{2\cdot7}$ to $Cs_2O_{3\cdot6}$, approaching Cs_2O_4; the variation in composition is probably due to the great reactivity of the amalgam with moisture.[3]

Red crystals of the monoxide, Cs_2O, are formed by partially oxidising cæsium and distilling off excess metal under reduced pressure.[1] The heat of formation for the reaction: $2Cs$ (solid) + $0\cdot5\ O_2$ (g) → Cs_2O (solid) is $\Delta H_{298} = -75\cdot9$kg.-cal.[4] Other values given are 83·2[1] and 82·7.[2] The monoxide is also formed by heating the peroxide, Cs_2O_2.[2] The total energy change due to the formation of the monoxide from its elements is 168kg.-cal.[2]

A study of the Cs–Cs_2O system in nitrogen shows the existence of a number of suboxides of cæsium: Cs_7O m.p. 3°C.; $2Cs_4O \rightleftharpoons Cs_7O_2$ + melt at 10°C.; $Cs_7O_2 \rightleftharpoons 2Cs_3O$ + melt at 50°C.; $Cs_3O \rightleftharpoons Cs_2O$ + melt at 170°C. There are also three eutectics; $Cs + Cs_7O$ at −2°C.; $Cs_7O + Cs_4O$ at −8°C. and $Cs_7O + Cs_7O_2$ at −12°C. There are apparently no solid solutions.[1,2]

The peroxide, Cs_2O_2, is obtained by allowing the requisite amount of oxygen to be absorbed by cæsium, contained in an aluminium boat in an evacuated glass apparatus, and then heating to the melting point and chilling rapidly. It is formed in an impure state by the rapid oxidation of a dilute solution of cæsium in liquid ammonia (see also page 2334), and, together with some monoxide, when the superoxide is partially decomposed. The heat of the reaction $2Cs$ (solid) + O_2 (gas) is 120·5kg.-cal. The heat of the dissociation, $2Cs_2O_2 \rightleftharpoons 2Cs_2O + O_2$, is 41·1kg.-cal.[2]

The trioxide is formed in a similar manner to the peroxide by the action of the calculated amount of oxygen on cæsium, by the oxidation of cæsium in air or by the incomplete dissociation of the superoxide. It is also formed, as a chocolate brown powder contaminated with peroxide and superoxide and traces of nitrate and nitrite, by the action of oxygen on a suspension of cæsium peroxide in liquid ammonia. The heat of formation for the reaction $2Cs$ (solid) + $1\cdot5O_2$ (gas) is about 126kg.-cal., and the heat of the dissociation, $2Cs_2O_3 \rightleftharpoons 2Cs_2O_2 + O_2$, is 29·7kg.-cal.[2]

The final oxidation product of caesium is the superoxide, 'tetroxide' or dioxide, CsO_2, and it is obtained at ordinary pressure by melting the metal in excess of oxygen. Reddish yellow crystals are obtained on slow cooling. At lower pressures a brown coloured product containing less oxygen is produced. Long shaking of a solution of cæsium in liquid ammonia with oxygen yields as the end product of oxidation CsO_2 with traces of nitrate and nitrite: $2Cs$ (solid) $+ 2O_2$ (gas) $\rightarrow Cs_2O_4 + 146{\cdot}46$ kg.-cal.[2] The so-called tetroxide, CsO_2, has been shown by Helms and Klemm to contain the superoxide ion O_2^- as in KO_2.[5]

A study of oxygen–caesium films has been made by Borzyak.[6] Wedge-shaped films of caesium on glass produced from a molecular beam have been oxidised with oxygen at liquid air temperature. The colourless transparent film obtained is shown to have the composition CsO_2 and to remain unchanged on heating to room temperature and above. A white film is also obtained by oxidation of caesium at room temperature. This contradicts the reference to the reddish-yellow colour of the superoxide. Treatment of this compound with cæsium vapour at 150–180°C. causes the colour of the film to become progressively yellower, whereas Cs_2O is described in the literature as red. The photoelectric sensitivity is at a maximum while the film is still yellow and although treatment of the superoxide with cæsium vapour at above 200°C. does produce a red colour the photoelectric sensitivity is lower than that of the yellow film. Either the statement about the red colour of CsO_2 is incorrect or the optimum photoelectric sensitivity is not linked with the composition Cs_2O. Electrochemical interactions of caesium and oxygen are described by Langmuir.[7]

When ozone is passed into a liquid ammonia solution of cæsium an ozonide is formed which cannot however be isolated free from ammonia.[8]

Theoretical calculations of the stability of solid and gaseous alkali oxides indicate that at 1000°K. all the gaseous alkali oxides with the exception of lithium monoxide are unstable and dissociate.[9]

No compound of argon and caesium is formed when an electric discharge is passed through liquid argon using a cæsium cathode.[2]

Caesium decomposes water, on which it floats, giving off hydrogen which burns with a red-violet flame. Water condensed as a white solid on cæsium cooled to −200°C. to −80°C. reacts with slow evolution of hydrogen; the reaction appears to begin at about −116°C.[2] The heat of formation, ΔH_{298}, for the reaction: Cs (solid) $+ H_2O$ (liquid) $\rightarrow CsOH$ (solid) $+ 0{\cdot}5H_2$ (gas) is $-28{\cdot}9$ kg.-cal.[4]

When an electrical discharge is passed through hydrogen at a gas pressure of 0·1 to 0·05 mm. and the hydrogen is allowed to flow through a nozzle 1 mm. in diameter into a mixing chamber where cæsium is heated to produce a vapour pressure of about 0·1 mm., a surface fluorescence, *i.e.* a blue light, already described by Bonhoeffer[10] is observed but the effect is transient. A four-hour exposure with cæsium at 200°C. produces no luminescence.[11] The mechanism of reactions involving excited electronic states with particular reference to the reactions of the alkali metals with hydrogen has been discussed by Magee and Taikei.[12] Some chemiluminescent and quenching reactions are considered. The reaction $M + 2H \rightarrow M^* + H_2$, where the asterisk denotes electronic excitation and the prime vibrational excitation, takes place readily with sodium at 200°C., slightly with potassium and apparently not at all with rubidium and cæsium.

Caesium hydride is formed when hydrogen is passed over heated cæsium or over the reduction product of cæsium carbonate and magnesium. The optimum temperature is 580°–620°C.[2]

The values obtained by Herold[13] for the dissociation pressures of cæsium hydride are given in Table I.

TABLE I.- DISSOCIATION PRESSURES OF CAESIUM HYDRIDE

Temp. °C.	Pressure, mm.Hg
377·5	520
349·5	209
308	44
288·5	19·7
266	6·85
245·5	2·55

The equation $\log p$ mm. = $-5900/T + 11{\cdot}79$ is also given. The calculated heat of formation of cæsium hydride from the above data is 13·48kg.-cal. per mole. The value given in Liquid Metals Handbook[4] for the reaction: Cs (solid) + $0{\cdot}5H_2 \rightarrow$ CsH (solid) is $\Delta H_{298} = -12$kg.-cal.

Caesium combines with deuterium in a similar way at 320°C. to form caesium deuteride, CsD.[2]

Hydrogenation of ethylene or carbon monoxide in the presence of cæsium as a catalyst occurs appreciably at room temperature and more rapidly at 200°C. The rate of combination with hydrogen is much retarded by the gradual formation of cæsium hydride.[14]

Nitrogen in its normal form does not react with cæsium.[2] According to Fischer and Schröter[15] when an electric discharge is passed between alkali metal electrodes through a liquid mixture of 90% argon and 10% nitrogen alkali metal nitrides are formed, but Moldenhauer and Mottig[16] have shown that nitrogen activated by an electric discharge reacts with the alkali metals, sodium, potassium, rubidium and caesium to form azides. With cæsium the product also contains a small quantity of nitride formed apparently by the decomposition of the azide.

Caesium in the molten state reacts with graphite, soot and active charcoal as already described for rubidium (see page 2175). The carbon swells up as it is permeated by metal and disintegrates giving out heat. It has been possible to isolate products of constant composition for a fixed range of temperature and pressure for the alkali metals potassium, rubidium and caesium, the last element giving the brown compound, CsC_8.[17] Schleede and Wellmann[18] have studied the structure of the above insertion or lamellar compounds; the brown product, CsC_8, has a layer lattice with cæsium planes alternating with the basal planes of graphite. On heating the brown compound to a higher temperature alternate metal layers are removed leaving behind the black compound CsC_{16}. Rüdorff and Schulze have obtained the following compounds: MC_{24}, MC_{36}, MC_{48} and MC_{60} by thermal decomposition of MC_8 where M is potassium or rubidium.[19] Herold[20] has studied the equilibria: $3C_8M \rightleftharpoons C_{24}M + 2M$, (where M = potassium, rubidium or caesium), attained by passing metal vapour at various temperatures up to 600°C. over graphite. The heat of the reaction, Q, where $C_{24}M + 2M$ (vapour) $\rightarrow 3C_8M + 2Q$, has been determined for all the above alkali compounds and in the case of cæsium is 10·1 kg.-cal.

The compound $CsHC_2$ is formed when dry acetylene is led into a liquid ammonia solution of cæsium; some ethylene is liberated. The rapid heating of this compound in a vacuum at about 300°C. yields transparent crystals of the carbide, Cs_2C_2, which is further decomposed at red heat to the metal and amorphous carbon.[2]

Caesium absorbs carbon monoxide even at low temperatures and pressures forming minute shining yellow spheres. They are insoluble in benzene, ether and ammonium hydroxide and decompose quietly with water. The composition corresponds to CsCO, probably $Cs_2C_2O_2$, because on dissolving the substance in dilute sulphuric acid and adding phenylhydrazine a precipitate of the diphenylhydrazone of glyoxal is obtained.[21]

Setton[22] has measured the heat liberated in the reaction: $n\text{Cs} + n\text{CO} \rightarrow (\text{CsCO})_n$ by direct determination in a differential calorimeter: $\Delta H = -37{\cdot}96$ kg.-cal. per g.atom of Cs. More recently Setton[23] has shown that cæsium gives a blue amorphous compound when it reacts with purified carbon monoxide. This compound decomposes violently at 250°C. forming resins, and its structural formula is believed to be O:C:C(OCs)Cs since acidification yields glycollic acid. If however the carbon monoxide contains traces of oxygen, a yellow amorphous compound CsC(:O)C(:O)Cs, stable up to 250°C., is obtained. This is a derivative of glyoxal, and the first compound, O:C:C(OCs)-Cs, is changed irreversibly to the second on treatment with oxygen.

Cæsium reacts with anhydrous hydrogen cyanide in benzene to form small white crystals of cæsium cyanide.[24]

Cæsium reacts with mercury to form amalgams (see page 2338).

Vanadyl trichloride, $VOCl_3$, reacts with cæsium even at room temperature; at 30°C. the reaction is very vigorous.[25]

The following heats of reaction are given for the action of fluorine and chlorine on cæsium: Cs (solid) + $0{\cdot}5\,F_2$ (gas) → CsF (solid); $\Delta H_{298} = -126{\cdot}9$kg.-cal.; Cs (solid) + $0{\cdot}5\,Cl_2$ (gas) → CsCl (solid); $\Delta H_{298} = -103{\cdot}5$ kg.-cal.[4]

When gaseous ammonia is passed over molten cæsium at 120°C., cæsium amide, $CsNH_2$, is formed.[2,26] The amide is a white crystalline solid.[26] The metal dissolves in liquid ammonia to form the blue solution characteristic of the alkali metals. There is no considerable heat effect and the solution is less dense than liquid ammonia; it conducts an electric current and is strongly paramagnetic. On standing in a closed tube the metal reacts gradually with liquid ammonia to form the amide and hydrogen. For a half saturated solution decomposition is complete in 1–2 hr.: with 0·3 g. Cs per ml. of liquid ammonia reaction is complete in 3 days.[2] The reaction is accelerated by raising the temperature, by introducing a catalyst such as platinum, iron, ferric nitrate or asbestos, and by exposure to ultra-violet light of short wavelength. Caesium is more reactive than the other alkali metals; the heavier the metal, the more readily it reacts.

In the presence of a catalyst, platinum black, on a bright day the reaction: $\text{Cs} + \text{NH}_3 \rightarrow \text{CsNH}_2 + \text{H}$ is complete in 0·25 hr.; under comparable conditions, for rubidium the time is 0·5 hr., for potassium 1·0 hr., and for sodium and lithium, several days.[26-28] The heat of formation of cæsium amide from its elements, Cs (solid) + $0{\cdot}5N_2$ (gas) + H_2 (gas) → $CsNH_2$ (solid), is 28 kg.-cal.[26] The heat of reaction, Cs (solid) + NH_3 (gas) → $CsNH_2$ + $0{\cdot}5H_2$ (gas), is 14·4 kg.-cal.[27] The amide is also formed together with cæsium peroxide, Cs_2O_2, and cæsium hydroxide when the metal is slowly oxidised in liquid ammonia. On warming, the mixture decomposes with a slight explosion into cæsium hydroxide, cæsium and nitrogen.[2]

Cæsium dissolves in methylamine, ethylamine and also in *iso*propylamine with reaction. It is also soluble in ethylenediamine. All the solutions are more or less unstable owing to the formation of substituted amides and hydrogen. As with liquid ammonia, the solutions are blue.[29]

When sulphur vapour reacts slowly with heated cæsium in an evacuated apparatus with agitation to prevent polysulphide formation, the monosulphide Cs_2S is formed.[2] Excess of metal is vaporised at 200°C. Using mercury sulphide, HgS, in place of sulphur, prevents the formation of polysulphides; on completion of the reaction excess metal and mercury are distilled off at

250°C. The monosulphide is a white solid, the disulphide yellowish brown, m.p. about 460°C.; the trisulphide red, m.p. 217°C.; the tetrasulphide dark red, m.p. above 160°C.; the pentasulphide also dark red, m.p. 210°C.; the hexasulphide brown, m.p. 186°C. The existence of these compounds was demonstrated as a result of thermal analysis of the cæsium–sulphur system by Biltz and Wilke-Dörfurt[30] in 1906. Pearson and Robinson[31] have reviewed the data on the polysulphides of the alkali metals and discussed the molecular structure. Caesium resembles potassium and rubidium in that the highest stable sulphide formed by the action of sulphur on the molten metal is Cs_2S_6, the highest stable sulphides of lithium and sodium being Li_2S_2 and Na_2S_5. The two most stable sulphides of all the alkali metals are the disulphide, e.g. Cs_2S_2, and in the case of potassium, rubidium and cæsium, the pentasulphide, Cs_2S_5. The amount of water of crystallisation and the solubility in alcohol and water decrease from lithium to cæsium. Sulphur reacts with the monosulphide of cæsium in solution to give Cs_2S_3,H_2O, Cs_2S_4,H_2O or Cs_2S_4 and Cs_2S_5. Desulphurisation of the hexasulphide in hydrogen yields the disulphide, Cs_2S_2; in nitrogen the trisulphide is obtained.

The heat of formation of cæsium monosulphide, 2Cs (solid) + S (solid) $\rightarrow$ Cs_2S (solid), at 25°C. is −81·1 kg.-cal.[4] (see also page 2334).

When hydrogen sulphide is led into toluene containing cæsium, cæsium hydrogen sulphide, CsHS, is obtained in the form of white needles.[32]

Cæsium reacts with selenium vapour to form cæsium selenide, Cs_2Se. The vapour is passed slowly over the metal contained in an evacuated apparatus and agitation is necessary to ensure that selenium is always in contact with uncombined metal. Excess of metal is distilled off at 200°C. leaving a white non-crystalline powder.[2] The monoselenide is also formed when mercuric selenide is used in place of sulphur, excess metal and mercury being distilled off when the reaction is completed.[33,34]

Cæsium monotelluride, formed in the same way as the selenide, is a pale yellow non-crystalline powder, m.p. 680°C. with decomposition.[33,34] The hydroselenide and hydrotelluride of cæsium are prepared by the action of hydrogen selenide or telluride on cæsium ethoxide. Air and moisture must be excluded. Crystalline compounds are obtained by distilling off the alcohol under reduced pressure.[35]

Cæsium combines with phosphorus when both are heated together in an evacuated vessel at 400–430°C. forming the reddish-brown compound Cs_2P_5.[2]

Glass is not attacked by pure cæsium heated in a vacuum at 100°C.; indeed cæsium vapour does not appear to attack ordinary glass below 300°C., and glass which is well out-gassed is scarcely attacked by cæsium vapour up to about 430°C. At this temperature the resistance of the glass decreases rapidly, the metal being absorbed in larger amounts, and the glass becoming brown. Quartz behaves similarly to glass.[2]

Molybdenum metal and borosilicate glass may be used to contain cæsium vapour: the point of fusion however must be kept below 280°C. It has been found that heating to 300°C. for 160 hr. causes a penetration of 1 mm. at the point of fusion and heating to 320°C. has the same effect within 50 hr.[36]

For the storage of cæsium in capillary tubes a sodium magnesium borosilicate glass has the advantage that when the end of the tube is sealed, cæsium reacts with the glass at the ends forming a vitreous material having a coefficient of expansion different from that of the intermediate portions of the tube, so that when it is necessary to liberate the contents of the tube the ends can be removed without shattering the whole body of the tube.[37]

The chemical composition of special glasses for high-vacuum technique and resistant to cæsium vapour is described by Knapp.[38] A detailed account of the properties of highly siliceous glasses in which cations, including

Na^+, K^+, Rb^+ and Cs^+, are "embedded" is given by Kühne *et al.*[39] Reactions of ions, including sodium and caesium ions, in aqueous solutions with glass and metal surfaces have been studied with radioactive tracers by Hensley, Long and Willard.[40]

Caesium metal dispersions stable against settling and agglomeration in which the dispersed metal does not exceed 50μ in size are obtained by preparing an emulsion of finely divided molten particles in an inert liquid hydrocarbon having a boiling point above the melting point of the metal in the presence of an emulsifying agent. The compounds suitable for emulsifying agents are complex addition compounds formed between (*a*) alkali metal alkoxides, MOR, where M is an alkali metal and R an aliphatic, *cyclo*aliphatic or aromatic radical and (*b*) an alkali metal organic compound in which the alkali metal atom is directly attached to an allylic residue, *i.e.* compounds having at least one residue of the structure C:CCM, where M is the alkali metal.[41]

The protection of phosphors, zinc cadmium sulphide, from attack by alkali metal vapours is described by Hushley and Siebert.[42] In order to prevent chemical reaction between the cathode-ray phosphor of an electric discharge tube and caesium vapour from the photoelectric surface of the tube, the phosphor is coated with the oxide SiO supported on aluminium.

Caesium is much more readily displaced from its salts by iron than is potassium or sodium.[43] The b.p. of the alkali metals are: Cs 670°C., Rb 696°C., K 757°C., Na 877°C. and Li 1400°C. When a mixture of caesium chloride and iron is heated at 900°C. for 2 hr. at reduced pressure a reversible reaction occurs: $Fe + 2CsCl \rightleftharpoons FeCl_2 + 2Cs$. The reaction from right to left apparently occurs in the gaseous phase because of the volatility of iron chloride. At a pressure of 0·001 mm. caesium hydroxide begins to react with iron at 500°C. to 550°C. liberating hydrogen: $3CsOH + 2Fe \rightarrow Fe_2O_3 + 3Cs + 1{\cdot}5H_2$. A yield of 50% of metal is obtained by heating for 2 hr. at 700°C.; probably a non-reducible ferrite is formed which prevents further action. Caesium is displaced from its sulphate by heating at low pressures with iron. The reaction begins at 800°C. and is rapid at 1000°C.: $2Cs_2SO_4 + 3Fe \rightarrow 4Cs + Fe_2O_3 + FeS + SO_2 + 1{\cdot}5O_2$. The metal is partially oxidised by the gas evolved in the reaction. Caesium is displaced from its carbonate by heating with iron in an evacuated vessel: $2Cs_2CO_3 + 2Fe \rightarrow Fe_2O_3 + CO + CO_2 + 4Cs$. The reaction begins at 650°C. and is rapid at 1000°C. After 1 hr. at 1000°C. a deposit of lightly oxidised cæsium is found in the cold end of the tube; 50% of the caesium in the carbonate is liberated. About 10% of the metal in caesium nitrate is liberated on heating with iron for half an hour at 600°C. A gas containing 10% of oxygen and 90% of nitrogen is given off. Nickel does not reduce the alkali metal oxides. The pressure at which the above reactions are carried out is generally of the order of 10 mm.

Accounts of the properties of the alkali metals have been given up to about 1936 by Guillet,[44] up to 1940 by Klemm[35] and up to 1948 by Sidgwick.[45]

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Reactions of Cæsium in Liquid Ammonia

Reactions of solutions of the alkali metals in liquid ammonia described in the literature up to about 1937 have been reviewed by Fernelius and Watt[1] and reactions of inorganic substances with liquid ammonia solutions of metals reported up to about 1950 are described by Watt.[2] In both reviews numerous references are given for lithium, sodium and potassium but only a few for rubidium and cæsium.

Early references show that the slow oxidation of cæsium in liquid ammonia with oxygen at −60°C. yields cæsium peroxide, Cs_2O_2, cæsium amide, $CsNH_2$, cæsium hydroxide and some cæsium nitrite and nitrate and that more rapid oxidation gives the peroxide, trioxide and tetroxide, now known to be CsO_2.[1,3]

A white gelatinous precipitate of cæsium hydroxide is formed when ozone is first led into a liquid ammonia solution of cæsium; the blue colour of the metal solution disappears and as the reaction continues the precipitate dissolves and a deep orange liquid and a second precipitate form. The compound formed is probably an ozonide; it is more stable than the product obtained with lithium, sodium, potassium or rubidium under the same conditions and contains nearly one atom of oxygen per molecule of cæsium hydroxide.[4]

The monosulphide, selenide and telluride of cæsium have been prepared

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by the direct interaction of the elements in liquid ammonia solutions of cæsium.[5,6]

Caesium hexasulphide, Cs_2S_6, prepared *in situ* in liquid ammonia, from the stoicheiometric amounts of the elements in the presence of the iodide, has been potentiometrically titrated with a standard solution of cæsium in liquid ammonia. Points of inflection on the titration curve correspond to the compositions Cs_2S_4 and Cs_2S_2. The dark yellow crystals of the disulphide are so sparingly soluble in liquid ammonia that further reaction with the metal solution to form the monosulphide is very slow.[7]

More recently Féher and Naused have prepared and isolated the crystalline polysulphides, Cs_2S_2, Cs_2S_3, Cs_2S_5 and Cs_2S_6, by allowing the calculated amounts of the elements to react together in liquid ammonia. The tetrasulphide cannot be obtained in this way.[8]

The heat of reaction of cæsium with ammonium ion in liquid ammonia at −33°C. has been measured by Coulter and Maybury,[9] using ammonium chloride and ammonium bromide in a liquid ammonia calorimeter. From the value obtained together with the heat of solution of the metal in pure liquid ammonia, the heat of reaction with the ammonium ion is calculated to be 41·6 kg.-cal. The mean value for the exothermic heats of reaction of lithium, sodium, potassium and cæsium is 40·4 ± 1 kg.-cal., which indicates a close similarity in the nature of the dilute solutions of these metals in liquid ammonia.

Boron trifluoride amine, BF_3,NH_3, has been treated with an excess of a solution of cæsium in liquid ammonia and the solution back-titrated with ammonium iodide. Caesium behaves like potassium, *i.e.* one atom of metal reacts with one molecule of the ammine. Hydrogen is evolved and the metal fluoride and the amide, BF_2NH_2, are formed.[10]

Nickel bromide, $NiBr_2$, is reduced to nickel by the action of cæsium in liquid ammonia. The rate of solution of the alkali metals in liquid ammonia and the rate of reaction with nickel bromide increase from lithium to cæsium, although with all the alkali metals the rates are too rapid for accurate measurement. The catalytic activity per unit area of the nickel produced is substantially constant whichever alkali metal is used to reduce the bromide.[11]

A brown-violet solution is obtained when cæsium reacts with lead in liquid ammonia.[12]

When acetylene is passed into a liquid ammonia solution of cæsium at −40°C. to −60°C., the monoacetylide, $CsHC_2$, is formed together with some ethylene:[1] $3C_2H_2 + 2Cs \rightarrow 2CsHC_2 + C_2H_4$.

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Organic Reactions of Cæsium

General accounts of organometallic compounds including those of the

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alkali metals have been given by Wooster,[1] Sidgwick[2] and Coates,[3] with many references to original papers.

Caesium reacts with diethyl zinc to give colourless caesium ethyl, soluble in diethyl zinc; it forms as an oily concentrated solution which quickly absorbs carbon dioxide and on further treatment with sulphuric acid yields propionic acid.[4]

The surface of caesium metal becomes black when treated with benzene or toluene in vacuum even at room temperatures. Above the melting point of the metal, the reaction is rapid with the formation of a black slimy mass which has been isolated by decanting off and washing with dry pentane. According to the early literature, since no hydrogen is evolved during the reaction the following change is suggested: $3C_6H_6 + 2Cs = 2CsPh + C_6H_8$.[5] Grosse considers that caesium phenyl is not formed in this reaction and draws attention to the fact that on treatment with water, diphenyl and not benzene is obtained.[4]

More recently de Postis[6] has investigated the action of caesium on aromatic hydrocarbons including benzene and toluene. The black compound formed with benzene is spontaneously inflammable in air and decomposes water giving off hydrogen. Its composition accords with the formula $C_6H_6Cs_6$; it is insoluble in all known neutral organic solvents but dissolves in liquid ammonia giving a ruby red colour which quickly turns green; on evaporation of the solvent ammonia black needles are formed identical in composition with the material formed by the direct reaction of the metal with benzene. The considerable encumbrance of the six caesium atoms around the benzene molecule explains why the compound appears to have the same properties as caesium metal.

Benzene, *tert.*-butyl benzene, and under certain experimental conditions cumene and diphenylmethane all attack caesium without evolution of hydrogen, giving sparingly soluble amorphous compounds which attack water giving off hydrogen, do not absorb carbon dioxide and behave generally as if they were only adsorption complexes of caesium on the hydrocarbon. They do not react with alkyl halides.

Toluene, the polymethyl benzenes, ethylbenzene, *iso*propylbenzene, tetrahydronaphthalene, diphenylmethane, allylbenzene and similar hydrocarbons all attack caesium, hydrogen being evolved in amounts corresponding reasonably with the amount of caesium taken up. Generally the products are soluble, they are destroyed by water regenerating the original hydrocarbon, they rapidly absorb carbon dioxide giving quantitatively the caesium salt of the organic acid and they react rapidly with alkyl halides producing methylation, benzylation and so on. For example with toluene the following series of reactions occurs: $PhMe + Cs \rightarrow PhCH_2Cs + 0{\cdot}5H_2$; $PhCH_2Cs + CO_2 \rightarrow PhCH_2COOCs$; $PhCH_2Cs + PhCH_2CCl \rightarrow PhCH_2CH_2Ph + CsCl$. The formation of caesium benzyl has been confirmed by gravimetric analysis. Analogous results have been obtained with xylene and mesitylene: $MeC_6H_4Me + Cs \rightarrow MeC_6H_4CH_2Cs + 0{\cdot}5H_2$; $Me_2C_6H_3Me + Cs \rightarrow Me_2C_6H_3CH_2Cs + 0{\cdot}5H_2$. With *iso*propylbenzene the action of caesium is somewhat constrained by the two extranuclear methyl groups, and under certain conditions an additive compound can also be obtained which cannot be carbonated. The formation of phenyl*iso*propyl caesium is represented by: $PhCHMe_2 + Cs \rightarrow PhCCsMe_2 + 0{\cdot}5H_2$, and subsequent carbonation by: $PhCCsMe_2 + CO_2 \rightarrow PhC(Me_2)COOCs$. The caesium compound obtained from xylene is a brown insoluble product, that from mesitylene orange-red and slightly soluble, while the *iso*propylbenzene compound with caesium is reddish brown and slightly soluble.

Pure diphenylmethane attacks caesium at 80–90°C. under vacuum; a blue coloration is first observed, then hydrogen is evolved followed by the formation of a brown product which can be carbonated. If the reaction is carried out in ether a product is formed which does not absorb carbon dioxide. A very rapid quantitative reaction occurs with caesium and allylbenzene in ether; the product is bright red and on carbonation gives cæsium phenyl*iso*crotonate which on treatment with acid yields the corresponding acid: $PhCH{:}CHCH_2$-COOH; on heating, this compound cyclises to *α*-naphthol.

Cæsium in benzene reacts with di-*n*-butyl mercury to give cæsium phenyl. Ordinary molecular hydrogen reduces cæsium phenyl at room temperature to benzene and cæsium hydride. The rates of reaction of the alkali metal phenyls with hydrogen already given (see page 2402) show that cæsium phenyl is more reactive than the other metal phenyls.[7]

In the presence of cæsium, ethylene is hydrogenated even at room temperature; at 200°C. hydrogenation proceeds at a greater rate but comes to a standstill after a short time owing to the formation of cæsium hydride.[8] Cæsium, obtained in a finely divided state from a liquid ammonia solution, catalyses the hydrogenation of ethylene at 200°C. at a medium rate for a longer time without change of efficiency. Of all the alkali metals, cæsium is the only one suitable for this reaction because its hydride is so readily dissociated.[9]

The reaction of cæsium with acetylene has already been described (see page 2330).

Phenylacetylene reacts with cæsium in ether to give cæsium phenylacetenyl. When 0·02 mol. of the hydrocarbon in 25 ml. of ether is added to 0·01 g. atom of alkali metal, the time required for reaction is 25 hr. for cæsium, 12 hr. for rubidium and 40 hr. for potassium. The cæsium compound, $PhC{\vdots}CCs$, like the rubidium derivative, is dark tan in colour. Carbonation of the metal phenylacetenyls followed by treatment with a mineral acid yields $PhC{\vdots}C$.-COOH. The time taken for the alkali metal phenylacetenyls to react with benzonitrile increases in the order: $PhC{\vdots}CCs$, $PhC{\vdots}CRb$, $PhC{\vdots}CK$, $PhC{\vdots}CNa$, $PhC{\vdots}CLi$. There is no significant reaction between the metal phenylacetenyls and ether during the time taken to add the benzonitrile.[10]

The relative reactivities of *n*-butyl chloride with the alkali metal derivatives of benzophenone show that the cæsium derivative is more reactive than the rubidium compound which in turn is more reactive than the potassium compound.[10]

Cæsium amalgam in ether reacts with triphenylmethyl chloride, Ph_3CCl, to give a deep blood-red solution of the metal derivative Ph_3CCs. The reaction apparently takes place in two stages, the free radical, Ph_3C, being first formed and then adding cæsium. The solid powdery product resembles the sodium, potassium and rubidium compounds. If dried in the complete absence of air, cæsium triphenylmethane will redissolve in ether; air and moisture decolorise the compound. Cæsium metal reacts with triphenylmethyl chloride in ether to form a yellow solution which gradually deposits white flocks; after a day, a deep brown-red precipitate is formed of a cæsium organic compound, and the solution becomes orange-red, different in colour from the blood-red of solutions of Ph_3CCs. Water in the absence of air immediately decolorises the substance.[4]

Cæsium vapour reacts fairly quickly with diethyl ether.[11]

An intensely blue, electrically conducting solution of cæsium is obtained in the dimethyl ether of ethylene glycol.[12]

Cæsium dissolves more readily in liquid methylamine and ethylamine than in liquid ammonia and gives similar blue solutions. The corresponding reaction with *iso*butylamine gives no blue solution.[5]

Cæsium reacts with alcohols in an evacuated system to form cæsium alkoxides. The solvated alkoxides formed are decomposed by warming the system: CsOMe,MeOH at room temperature; CsOEt,EtOH at 50°C.; CsOPr,PrOH at 100°C. On heating at 330°C., the following reaction occurs: $6CsOMe \rightarrow 9H_2 + 2Cs_2CO_3 + 4C + 2Cs$. Addition of water to the residue from the incomplete pyrolysis of the methoxide gives a resin. Similar treatment with CsOEt gives a resin and the hydroxide, CsOH. The gases given off in moles per mole of caesium ethoxide, gas evolution being complete for each stepwise reaction, are as follows: at 225°C., $0{\cdot}976H_2$ and $0{\cdot}029C_2H_4$; at 245°C., $0{\cdot}027H_2$ and $0{\cdot}073C_2H_4$; at 280°C., $0{\cdot}223H_2$ and $0{\cdot}178C_2H_4$. Caesium propoxide, CsOPr, begins to decompose at 250°C. and the gas evolved by prolonged heating at 260°C. is almost pure hydrogen.[13]

When caesium is added to chloroform and the mixture is allowed to stand for a short time a vigorous explosion occurs.[14]

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CAESIUM ALLOYS

Alloys of caesium with lithium, sodium, potassium and rubidium have already been described under the heading of 'Alloys' with the appropriate alkali metal.

The intermediate phase poorest in alkali metal in the caesium–cadmium system is the crystalline cubic compound, $CsCd_{13}$ having the side of the lattice, $a = 13{\cdot}89$ A. There are 112 atoms in the unit cell, the alkali atoms being surrounded by 24 equally distant cadmium atoms. *X*-Ray evidence, density and analytical data show that the compound is definitely $CsCd_{13}$ and not $CsCd_{11}$ or $CsCd_{12}$. Powder diagram data have been given.[1]

The liquidus curve for caesium–mercury alloys shows three maxima corresponding to the compounds $CsHg_2$, (75·13% Hg); $CsHg_4$ (85·80% Hg) and $CsHg_6$ (90·06% Hg). The following compounds are indicated by the cooling curve: Cs_2Hg_3, $CsHg_2$, $CsHg_4$, $CsHg_6$, $CsHg_{10}$ (?), $CsHg_{12}$ (?).[2-4]

The melting points given are: $CsHg_2$, 208°C.; $CsHg_4$, 164°C. decomp.; $CsHg_6$, 158°C.; $CsHg_{10}$, 73°C.[2,3] The light alkali metals do not form compounds as rich in mercury as the heavy ones. From the phase diagrams and the melting points of the alkali metal–mercury diagrams it is found that the m.p. of comparable compounds falls with increasing atomic number of the alkali metal. Methods used for the detection of intermetallic compounds e.g. *X*-ray investigation, thermal expansion, determination of electrical resistance and of magnetic properties as a function of concentration and temperature are discussed by Grube[2] and reference is made to the alkali metal–mercury systems including that of caesium.

Bent and Hildebrand[5] have measured the vapour pressures of cæsium amalgam from 281°C. to 378°C. by a relative method against pure mercury. The activity of mercury in the amalgam is plotted against the molar fraction, showing the deviation from Raoult's law. The partial molar heat content of mercury is calculated from the temperature coefficient of the vapour pressures of the amalgams. This gives the free energy of transfer of mercury in amalgams over the range 281°C. to 378°C. The activity of the alkali metal has been calculated from the known activity of the mercury.

The e.m.f. of a cell in which the reaction is a transfer of one g.-atom of caesium to amalgam is 1·71 V. at 25°C. The deviations from Raoult's law expressed as β in the expression $\log a_1/N_1 = \beta N_2^2$ have been plotted against temperature and the same value for β found for Cs–Hg at 497°C., K–Hg at 307°C., Na–Hg at 25°C.

Kubaschewski and Catterall[6] have used the results of Bent and Hildebrand[5] to evaluate heat and entropy values. The data are somewhat uncertain but are given in Table II.

TABLE II.- HEAT AND ENTROPY VALUES FOR Cs–Hg SYSTEM

N_{Hg}	$\Delta\bar{G}_{\mathrm{Hg}}$ 610°K.	$\Delta\bar{H}_{\mathrm{Hg}}$	$\Delta\bar{S}_{\mathrm{Hg}}$	ΔV_{298}
0·90	−480	(− 450)	+0·05	−0·105
0·85	−1020	(−1100)	−0·11	(−0·15)
0·80	−1670	(−2070)	−0·65	(−0·13)
0·75	−2680	(−3400)	−1·18	
0·70	−3440	(−5200)	−2·88	

$\Delta\bar{G}_{\mathrm{Hg}}$, $\Delta\bar{H}_{\mathrm{Hg}}$ and $\Delta\bar{S}_{\mathrm{Hg}}$ are respectively the partial free energy, partial heat of solution and partial entropy in solution in calories when 1 g.-atom of mercury is assimilated by a theoretically infinite amount of an alloy of constant composition. ΔV_{298} is (volume of alloy − Σ volume of metals)/Σ volume of metals at 298°K. Values shown in parentheses are uncertain.

The electrical conductivity of caesium–amalgams is shown in Table III.

TABLE III.- ELECTRICAL CONDUCTIVITY OF CAESIUM–AMALGAMS

At.% Cs	Wt.-% Cs	Specific Conductivity $\kappa_{18°\mathrm{C.}} \times 10^{-4}$	Relative Conductivity 20°C.	40°C.	60°C.	80°C.
0·000	0·000	1·0462	1·000	1·000	1·000	1·000
0·060	0·040	1·0409	0·9948	0·9952	0·9953	0·9947
0·120	0·079	1·0346	0·9890	0·9898	0·9893	0·9879

The addition of caesium to mercury lowers the conductivity.[7]

The surface tension of dilute caesium amalgams is related to the activity of the dissolved metal by the expression $d\sigma/d(\log a_2) = K$ where a_2 is the activity and σ is the surface tension. Caesium atoms alone occupy the surface of caesium amalgams.[8]

Bering and Pokrovskii[9] describe a method for the measurement of the surface tension of alkali–metal amalgams by observation of the maximum pressure of drops in vacuo. The results given in Table IV are due to Semochenko, Bering *et al.*[10]

The thermal expansion coefficient of cæsium amalgam from the f.p. to 30°C. increases linearly with concentration at a greater rate for cæsium than for potassium amalgam. The specific volume increases linearly with concentration. The deduced atomic volumes of cæsium and potassium differ by only

TABLE IV.- SURFACE TENSION OF CAESIUM-AMALGAMS

Concentration g.-atom/l.	Surface Tension dyne/cm.
0·000708	404
0·000810	393
0·000918	286
0·00180	271
0·00297	260
0·00409	262
0·00533	256
0·01053	254
0·01066	250
0·0359	228
0·0535	229

10% and are respectively 50 and 30% less than in the pure metal. The contraction decreases with increasing temperature. The viscosity of cæsium amalgam is represented by the equation $\eta = \eta_0$ exp. q/RT with η_0 independent of temperature. For pure mercury q = 657·9g.-cal.; for cæsium amalgam containing 0·191 at.%Cs, q = 690·4g.-cal.[11]

When pollucite (1 part) is heated in a vacuum furnace at 900°C. with calcium (3 parts), cæsium is obtained, but if more calcium is used a non-volatile calcium–cæsium alloy is formed.[12]

The reaction between acid solutions and cæsium amalgam has been studied by Fraenkel *et al.*[13] Reproducibility of results is difficult to obtain because many variable factors are involved. If platinised platinum is used instead of smooth platinum against a *N.* calomel electrode, consistent results are obtained for the e.m.f. The rate of reaction is dependent on the hydrogen ion concentration, on the rate of stirring, and on the volume and surface area of the amalgams.

When silicon or germanium is heated with excess of cæsium at 600°C. to 700°C. in an inert atmosphere and the excess of metal distilled off in vacuo, a crystalline compound is obtained, with one atom of silicon or germanium per atom of cæsium, *i.e.* CsSi or CsGe. These compounds are decomposed by acids, alkalis or water. On heating in a vacuum the compound CsSi is decomposed to $CsSi_8$.[14] The degradation product of CsGe by thermal decomposition in a vacuum appears by *X*-ray studies to be $CsGe_4$. The crystal lattices of CsSi and CsGe are cubic with sides a = 13·51 and 13·67A. respectively. There are 32 molecules per cell and the experimental and *X*-ray densities are respectively 3·48, 3·45 for CsSi and 4·28 and 4·31 for CsGe. Whether or not there is any relation between these compounds and those of graphite is not yet known.[15]

The sensitivity of phosphorus and arsenic compounds of the alkali metals towards air and moisture, the attack by these compounds on the container materials and the relatively high dissociation pressures cause difficulties when attempts are made to prepare homogeneous substances by thermal decomposition. The compound Cs_3P has not yet been prepared. When cæsium vapour is allowed to react with red phosphorus small black needles of the approximate composition CsP_{10} are obtained. The compound Cs_2P_5 is considered to be a polyanionic compound similar to the polysulphides.[15]

Jack and Wachtel[16] have prepared cæsium–antimony alloys by heating cæsium vapour with antimony powder at 200°C.–210°C. for 10hr. in a hard glass tube previously evacuated to about 5×10^{-7}mm. The antimony powder increased in volume and changed colour from metallic gray to black. Caesium antimonide is described as the most efficient photo-emitter known and has found wide application wherever photomultipliers and photocells are used. The above authors give many references to earlier work on the exceptional photo-electrical properties of caesium antimonide and have themselves carried out an *X*-ray investigation of its crystal structure. The cæsium antimonide of composition Cs_3Sb was the only one to give *X*-ray photographs suitable for detailed structural analysis. Caesium antimonide has been shown to be a "normal valency" intermetallic compound with a small range of homogeneity near to the composition Cs_3Sb. The cubic unit cell has $a = 9{\cdot}147 \pm 0{\cdot}001$ A. The semi-conducting properties of the antimonide are explained by a filled Brillouin zone containing two electrons per atom. The photoemissivity of the antimonide is also discussed.

The semi-conductor properties of the system cæsium–antimony have been investigated by Suhrmann and Kangro[17] who give a plot of log κ (conductivity) versus $1/T$ for Cs_3Sb. The valence electrons of this compound are not as firmly held as in the corresponding potassium alloy, K_3Sb. Sommer[18],[19] had previously shown that the specific resistance of the cæsium alloy is of the order of 1 ohm per cm.-cube which is 10^5 times that of metals and normal alloys, and that it must be classed as a semi-conductor.

The molar volume of Cs_3Sb is given as 116, whereas the sum of the atomic volumes of the components is 219. The calculated molar volume of Cs_3Sb, assuming that it has a salt-like structure, is 138 whereas the calculated value assuming it to be an intermetallic compound is 117.[15]

Specimens of the composition Cs_2Sb have been prepared by Jack and Wachtel;[16] *X*-ray examination shows the presence of cæsium antimonide, Cs_3Sb, with some free metallic antimony, the side of the cubic lattice being about 9·14 A. A sample corresponding to the composition Cs_4Sb gives very diffuse reflections of the antimonide, and a cubic lattice side of 9·19 A. This specimen presumably contains free caesium. Compounds of composition Cs_3Sb_7 or Cs_2Sb_5 are probably poly-compounds.[15]

Caesium–indium films, like cæsium–antimony films, are shown by Suhrmann and Kangro[17] to have a negative electrical resistance coefficient.

The caesium–bismuth system contains several phases, Cs_3Bi, $CsBi_2$ and CsBi. The compound Cs_3Bi has a typical intermetallic structure; its molar volume, 121, is much less than the sum of the atomic volumes of its components, 219. The calculated values for a salt-like or ionic structure and for an intermetallic compound are 138 and 117 respectively. The composition, $CsBi_2$, also has the cubic structure of an intermetallic compound; its molar volume is 70·0 whereas the sum of the atomic volumes is 108 and the calculated values for an ionic structure and for an intermetallic compound are 80 and 71 respectively. A much greater difference in electronegativity of the two components of an alloy and a stronger contraction of molar volume occur for cubic than for hexagonal structures. A much lower electronegativity difference and lower % contraction of the free atoms are shown for the hexagonal structures, $CaLi_2$, $TiBe_2$, $CaMg_2$ and $BaMg_2$, than for the cubic structures, $CaAl_2$, KBi_2, $RbBi_2$ and $CsBi_2$.[15]

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SECTION LXXXIV

CAESIUM HYDRIDE

By N. M. HOPKIN

Cæsium hydride is prepared[1] by heating cæsium carbonate with magnesium in the presence of hydrogen. The reaction with magnesium takes place at 300°C. and the cæsium vapour combines with hydrogen at 580–620°C.; after 26 hr. 48% of the cæsium will have formed the hydride. Cæsium deuteride[2,3] can be prepared by reducing deuterium oxide with iron and causing the deuterium to react with freshly distilled cæsium. The reaction with deuterium takes place at 360°C., but it is slower than that for hydrogen. The dissociation pressures can be calculated from the equation:- $\log p = (a/T) + b$ where a and b are $-3475{\cdot}5$ and $7{\cdot}50$ for the hydride and $-2695{\cdot}5$ and $8{\cdot}68$ for the deuteride respectively. These differences suggest a method for separating the isotopes of hydrogen. The heat of formation for cæsium deuteride is 17,700 kg.-cal. Cæsium hydride can also be prepared[4] by mixing the molten metal with finely-divided sodium hydride and 0·1 to 1·0 wt.-% of fatty acid containing more than 8 carbon atoms, e.g. stearic, oleic, or palmitic acid etc. or one of their metal salts. Hydrogen is introduced and the reaction maintained at 200–450°C. A hydrocarbon with more than 8 carbon atoms, e.g. *iso*propylbenzene, which forms a hydrocarbide with the alkali metal, may be used instead of the fatty acid. In this case the vapours of the hydrocarbon are introduced into the stream of hydrogen entering the reactor.

Cæsium hydride has also been prepared[5] by introducing finely divided pure cæsium into the reaction vessel by distillation and allowing it to react with pure hydrogen generated *in situ* by the decomposition of potassium hydride. Cæsium reacted below its m.p. with 0·53 c.c. of combined hydrogen per sq. cm. of surface area per hr. at 100°C. The hydride did not dissolve in the cæsium metal up to 150°C. Pure hydrides free from the metal can be prepared at 3 atm. and 50°C.

The density[6] of cæsium hydride has been determined pycnometrically and found to be 3·42 ± 0·1. The previous values of Moissan are too low. When hydrogen is taken up considerable contraction of the lattice, 44·9%, takes place; it is greater in the case of the alkali metals than it is with the alkaline earth hydrides. The radius of the H ion is 1·45 A.

The latent heat[7] of sublimation has been calculated for cæsium hydride from spectroscopic and thermochemical data and the following figures are given. The heat of formation of cæsium hydride is 12·0, the latent heat of sublimation 38·5, and the heat of dissociation 43·8 kg.-cal./mole. The figures for rubidium hydride are similar, but the latent heat of sublimation is slightly higher.

The calculated dipole moment[8] of cæsium hydride is 7·47 debyes, and the corresponding lattice energy[9] is 154 kg.-cal. when Hyleeraas' value for the electron affinity for H^- of 17 ± 1 kg.-cal. is used. When cæsium atoms are adsorbed on calcium fluoride films they readily adsorb hydrogen,[10] which is liberated when irradiated with light of wave-length 2500–3000 A. The adsorption is at a considerably longer wave-length than for the alkali metal halides because of the low electron affinity of the hydrogen atom.

The interatomic distance[11] in the cæsium hydride molecule has been calculated from spectroscopic data and is found to be 2·494 A. The dissociation pressure of cæsium deuteride[12] increases more rapidly with increasing temperature than does cæsium hydride. The dissociation pressure is within ±2 mm. Hg up to 210°C., but at 320°C. it is 80·4 mm. Hg for cæsium deuteride and only 36·0 mm. Hg for cæsium hydride. The experimental values for cæsium hydride in the temperature range 245·5°C.–415·5°C. fit the equation:[13]

$$\log p = -\frac{5900}{T} + 11{\cdot}79$$

The heat of formation was calculated to be 13,940 g.-cal. for cæsium hydride.

Application

If cæsium is heated with a metal halide above the m.p. of the halide in the presence of hydrogen, but below the dissociation temperature of cæsium hydride, a stable solid solution[14] of the hydride in the halide is formed. This is less hazardous to handle than the free hydride and can be used as a drying or reducing agent.

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SECTION LXXXV

CAESIUM OXIDES AND HYDROXIDE

By L. F. WILSON

CAESIUM OXIDES

The following oxides of caesium are known;

Cs_2O – caesium monoxide.
Cs_2O_2 – caesium peroxide.
Cs_2O_3 – caesium sesquioxide.
CsO_2 – caesium superoxide.

In general these oxides are very similar to the corresponding oxides of rubidium and they are prepared by methods analogous to those used for rubidium oxides.[1-5] Complete oxidation of caesium metal in air produces the superoxide. The lower oxides are prepared by controlled oxidation of the metal, either in the solid state or in liquid ammonia solution.

In addition to the normal oxides of caesium, suboxides having the general formula Cs_xO, where $x > 2$, have been reported.[6] The caesium–oxygen system has been studied in the range Cs–Cs_2O by measurements affording temperature–resistance curves and by *X*-ray diffraction techniques.[7] The various suboxide compositions were prepared by incomplete oxidation of the metal and by addition of the metal to the monoxide. The phase diagram for the system is given in Fig. 1 and is essentially the same as that given by Rengade.[6] The existence of four suboxides, Cs_7O, Cs_4O, Cs_7O_2 and Cs_3O, and a eutectic point at the composition $CsO_{0\cdot099}$, is confirmed.

Cæsium monoxide has a reddish-brown colour in the cold and becomes dark brown when hot. *X*-Ray powder diffraction studies suggest that the compound crystallises in the hexagonal system with the anti-cadmium chloride, $CdCl_2$, type structure.[1] Single crystals of caesium monoxide have been prepared.[8] They are orange-yellow in colour, show a tendency to develop basal planes and exhibit shearing disorder when freshly pulverised. Single crystal *X*-ray diffraction studies confirm that the structure is of the anti-cadmium chloride type. The space group is D_3^5 and the hexagonal unit cell has the dimensions $a = 4\cdot256$ A. and $c = 18\cdot99$ A. The caesium–oxygen distance in the lattice is 3·01 A. and the caesium–caesium distance is 3·77 A.[8]

The melting points, dissociation temperatures at atmospheric pressure, and heats of formation of caesium peroxide, sesquioxide and superoxide are given in Table I.[2,3]

TABLE I.- MELTING POINTS, DISSOCIATION TEMPERATURES AND HEATS OF FORMATION OF CAESIUM OXIDES

Oxide	m.p.	Dissociation temperature	Heat of formation
Cs_2O_2	594°C.	1074°C.	120·5 kg.-cal./mole
Cs_2O_3	502°C.	1060°C.	126·0 kg.-cal./mole
CsO_2	432°C.	1265°C.	141·0 kg.-cal./mole

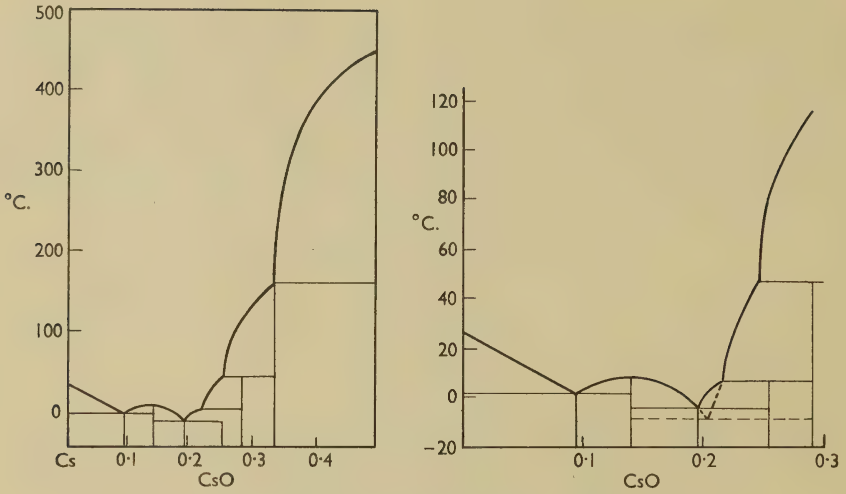

FIG. 1.- PHASE DIAGRAM FOR SYSTEM $Cs-Cs_2O$

The reactions $4CsO_2 \rightleftharpoons 2Cs_2O_3 + O_2 \rightleftharpoons 4Cs_2O_2 + 2O_2$ are reversible only within certain temperature limits outside which association does not take place.[2]

Cæsium sesquioxide crystallises in the cubic system, $a = 9{\cdot}86$A., and the structure is of the anti-thorium phosphide, Th_3P_4, type. The density, calculated from the unit cell dimensions, is 4·25. As in the case of rubidium magnetic susceptibility measurements on the sesquioxide suggest that the true formula is Cs_4O_6 or $Cs_4(O_2)_3$. One oxygen group carries a double negative charge and the other two carry single negative charges, the cæsium–oxygen distances being 3·74A. and 3·12A. An explanation of the dark colour of caesium sesquioxide has been proposed in terms of the electronic structure.[9,10]

The colours of the alkali metal superoxides deepen as the atomic number of the metal increases and caesium superoxide is reddish-yellow. The compound is paramagnetic and the magnetic susceptibility is $27{\cdot}3 \times 10^{-6}$ and $9{\cdot}3 \times 10^{-6}$ at −183°C. and 25°C. respectively.[5] The compound crystallises in the tetragonal system, $a = 6{\cdot}28$A., $c = 7{\cdot}24$A., and the structure is of the calcium carbide type.

Cæsium amalgam is spontaneously oxidised by air or oxygen at room temperature.[11] The reaction is complete in four to seven days and gives oxides of the composition $Cs_2O_{2\cdot7}$–$Cs_2O_{3\cdot6}$. The cæsium oxides thus formed oxidise some of the mercury of the amalgam to mercuric oxide.

The reaction between oxygen containing some ozone and cæsium hydroxide gives an orange coloured product which contains active oxygen.[12] If the gas used is anhydrous, the reaction is very slow, and moisture appears to play an important part.[13] Extraction of the ozonised cæsium hydroxide with liquid ammonia and evaporation to dryness gives a red solid containing 64–67% of caesium ozonide, CsO_3, the rest being caesium hydroxide.

The ozonide reacts violently with water and acids yielding oxygen, flashes of light accompanying the decomposition. The compound liberates iodine from an acidified potassium iodide solution but otherwise gives negative tests for peroxides. The decomposition of cæsium ozonide at room temperature is very slow, but on heating to 170°C. the compound decomposes into a mixture of a white and a yellow solid which gives the tests expected for caesium superoxide.

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CAESIUM HYDROXIDE

Caesium hydroxide is prepared by methods similar to those used for the preparation of rubidium hydroxide.[1,2] Small quantities of caesium hydroxide are readily obtained using the cell described by Thomas.[3] The electrodes are mercury and the process is made continuous by circulating the caesium amalgam from the cathode pool through a tube, where it is decomposed by water to give caesium hydroxide, and returning the mercury to the cathode. Evaporation of the hydroxide solution at 180°C. gives the monohydrate, $CsOH,H_2O$, which can be dehydrated by heating for an hour at 400°C. in vacuo.

The lattice energy of caesium hydroxide is 136 kg.-cal./mole.[4] The limiting conductivity of an aqueous solution of caesium hydroxide is 269·5.[5] Values of the density, equivalent conductivity, Λ, and activity coefficient, γ, of caesium hydroxide solutions are given in Table I.

TABLE I.- DENSITY, EQUIVALENT CONDUCTIVITY AND ACTIVITY COEFFICIENT OF AQUEOUS SOLUTIONS OF CAESIUM HYDROXIDE

concentration (moles/litre)	ρ	Λ	γ
0·000693	0·9972	264·5	
0·001537	0·9973	264·8	
0·002332	0·9974	265·9	
0·004081	0·9976	264·5	
0·006159	0·9979	265·2	
0·008376	0·9982	263·9	
0·01016	0·9984		0·905
0·01039	0·9985	262·6	
0·02044	0·9997		0·876
0·02550	1·0003		0·365
0·02751	1·0007	254·6	
0·05	1·0034		0·831
0·06532	1·0057	249·4	
0·9065	1·0087		0·800
0·1	1·0100		0·795
0·232	1·0270		0·759
0·38	1·0458		0·750

continued on following page

TABLE I.- CONTINUED

concentration (moles/litre)	ρ	Λ	γ
0·54	1·0659		0·753
0·89	1·1099		0·782
1·00	1·1238		0·795
1·32	1·1626		0·838

Cæsium hydroxide reacts with nitric oxide to give cæsium nitrite and a mixture of nitrous oxide and nitrogen.[7] The rate of reaction increases with temperature and at about 250°C. the proportion of nitrogen in the gaseous product increases. The reactions appear to be:

$$4NO + 2CsOH \rightarrow N_2O + 2CsNO_2 + H_2O$$
$$\text{and } 6NO + 4CsOH \rightarrow N_2 + 4CsNO_2 + 2H_2O$$

There seems also to be a secondary reaction in which the nitrous oxide is decomposed by the cæsium hydroxide.

Carbon monoxide reacts with solid cæsium hydroxide at atmospheric pressure and elevated temperatures, forming cæsium formate, oxalate and carbonate.[3,8] Between 275°C. and 296°C. the reaction is exothermic and up to 91% of the theoretical yield of cæsium formate is obtained. At higher temperatures the formate begins to decompose giving cæsium carbonate, carbon monoxide and hydrogen. Above 350°C. formation of cæsium oxalate occurs and the maximum yield of oxalate, 11·5%, is obtained at 410°C.

Cæsium hydroxide forms two brownish-yellow addition compounds with osmium tetroxide, $OsO_4,CsOH$ and $2OsO_4,CsOH$.[9,10] The compounds are thermally unstable and easily hydrolysed in solution.

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SECTION LXXXVI

CAESIUM FLUORIDE

By L. F. WILSON

The melting point of cæsium fluoride, CsF, is 684°C. and the boiling point is 1251°C.[1] The vapour pressure of the salt from 955°C. to the b.p. is given by the expression

$$\log p(\text{atm.}) = \frac{-34{,}700}{4{\cdot}57t + 4{\cdot}982}.$$

Observed values of the vapour pressure in this temperature range are given below.[1]

t(°C.)	955	1046	1118	1122	1204	1205	1251
p(mm.)	75·6	133·5	253·2	261·2	524·7	528·7	759·2

Vapour density determinations indicate that cæsium fluoride exists as individual molecules in the vapour state.[2] The heat of formation of the compound is 135kg.-cal./mole,[3] the standard free energy of hydration is 167 kg.-cal./mole,[4] and the heat of solvation is 180kg.-cal./mole.[5] The dissociation energy is calculated as 130kg.-cal./mole.[6]

Cæsium fluoride is readily soluble in water, 85·65g. dissolving in 100 ml.[7] The solubility in acetone was reported by Lannung[8] to be 0·077% at 18°C. and 0·087% at 37°C. Mysels[9] replotted the conductivity data given by Lannung and extrapolated to zero conductivity at a moisture content of 0·2–0·3%, less than that of Lannung's 'anhydrous' acetone. Mysels suggests that in anhydrous acetone the conductivity is very close to zero. If this is correct the conductivity of a saturated solution of cæsium fluoride in acetone could be used to determine small amounts of water in acetone.[9] The solubility of cæsium fluoride in bromine trifluoride is 3·68% at 25°C. and 4·67% at 70°C.[10] Accurate comparisons of the lattice constants of pure ice and ice contaminated with cæsium fluoride indicate that the fluoride ion enters the crystal lattice of the ice substitutionally.[11]

Study of the cæsium–cæsium fluoride system shows that complete miscibility occurs above the m.p. of cæsium fluoride.[12] The solubility of the fluoride in liquid cæsium metal, at a given temperature, is greater than the solubility of the other alkali metal fluorides in the respective metals.

Cæsium fluoride reacts with the trifluorides of the rare-earth metals to form compounds of the type $3CsF,MF_3$, where M is a rare-earth metal. In the cæsium fluoride–yttrium fluoride system a eutectic occurs at 673°C. and 96mol.-% YF_3; the compound $3CsF,YF_3$ melts congruently at 1075°C.[13] Systems of cæsium fluoride with the fluorides of erbium, samarium, praseodymium and lanthanum show eutectics at 648°C., 645°C., 635°C. and 600°C. respectively.[13,14] The compounds $3CsF,ErF_3$, $3CsF,SmF_3$, $3CsF,PrF_3$ and $3CsF,LaF_3$ melt at 1048°C., 972°C., 920°C. and 795°C. respectively. The thermal stability of double fluorides of the type $3M'F,M'''F$, where M' is an alkali metal and M''' a trivalent metal, increases with increasing radius of the alkali metal ion and reaches a maximum for double fluorides containing caesium.[13]

Complex fluorides of the type $CsM''F_3$, where M″ represents calcium, magnesium or zinc, are formed by the reaction of cæsium fluoride with the oxides of the divalent metals at temperatures in the range 500–800°C.[15] The double fluorides may also be synthesised from the component fluorides. The structures of these compounds are modifications of the perovskite structure: $CsCaF_3$ crystallises in the cubic system, with a = 4·54A.; $CsMgF_3$ and $CsZnF_3$ are tetragonal with lattice constants a = 9·37A., c = 8·70A. and a = 9·88A., c = 9·03A., respectively.

Cæsium fluoride, like rubidium fluoride, forms compounds with the caesium salts of some oxy-acids. The compounds that have been characterised are:

CsF,Cs_2CrO_4[16] CsF,Cs_2SO_4[17]
CsF,Cs_2MoO_4 $2CsF,3Cs_2Ti_2O_5$[18]
CsF,Cs_2WO_4

The compound $2CsF,3Cs_2Ti_2O_5$ decomposes at room temperature. Cæsium fluoride gives a simple eutectic with cæsium carbonate; no compounds are formed.[18] In the cæsium fluoride–molybdenum trioxide system the congruently-melting compound $Cs_3MoO_3F_3$ is formed;[17] it crystallises in the cubic system and readily hydrolyses to give Cs_3MoO_4F.

Cæsium perfluorides are formed by the reaction of caesium chloride with fluorine. Their properties are closely similar to those of the corresponding rubidium compounds, but the cæsium compounds are more stable and are not decomposed at 300°C.[19,20]

Cæsium fluoride, like the fluorides of potassium and rubidium, forms a series of acid fluorides. A study, by the freezing point method, of the cæsium fluoride–hydrogen fluoride system indicates the existence of four acid fluorides; CsF,HF, CsF,2HF, CsF,3HF and CsF,6HF.[21] The melting points of these compounds, and the eutectic points between them, are given in Table I, the melting point diagram for the system being shown in Fig. 1.

TABLE I.- THE SYSTEM CAESIUM FLUORIDE–HYDROGEN FLUORIDE

t(°C.)	Mol.-% HF	Solid Phase
−50	83	CsF,6HF
−42·3 (m.p.)	85·7	CsF,6HF
−49·5	82·8	CsF,6HF CsF,3HF
−30	82	CsF,3HF
0	80	CsF,3HF
20	78	CsF,3HF
32·6 (m.p.)	75	CsF,3HF
16·9	70·9	CsF,3HF CsF,2HF
30	70	CsF,2HF
50·2 (m.p.)	66·7	CsF,2HF
38·3	63·9	CsF,2HF CsF,HF
60	60	CsF,HF
100	57	CsF,HF
150	53	CsF,HF
176 (m.p.)	53·0	CsF,HF
151·5	45·3	CsF,HF

The compound CsF,HF exists in at least two forms within the temperature

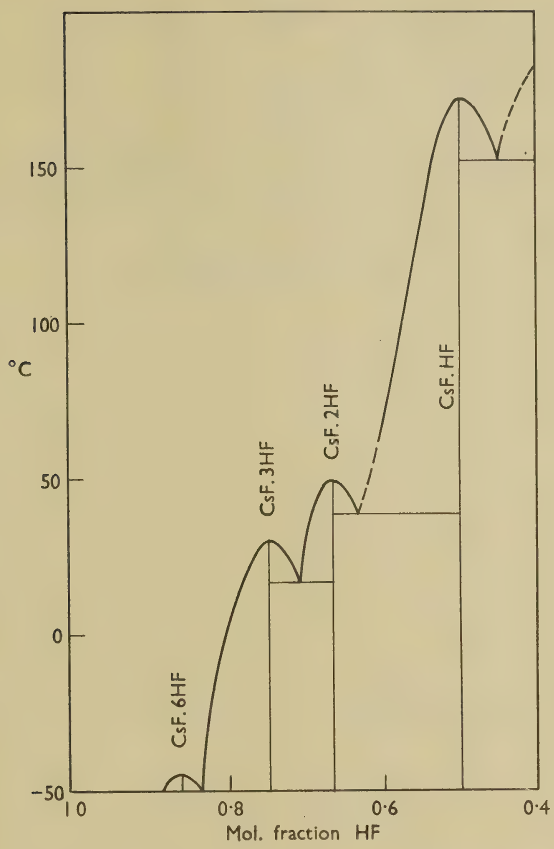

FIG. 1.- THE SYSTEM CsF–HF

range from 30°C. to the m.p., 176°C.

A comparison of the acid fluorides of the alkali metals reveals the following trends with increasing atomic number of the metal:[21]

i. The melting point of corresponding compounds decreases, e.g. NaF,HF m.p. 278°C., KF,HF m.p. 239° C., RbF,HF m.p. 205°C. and CsF,HF m.p. 176°C.
ii. The corresponding compounds are more stable.
iii. The maximum number of molecules of hydrogen fluoride that can combine with the metal fluoride increases.

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SECTION LXXXVII

CAESIUM CHLORIDE

By R. S. MILNER and L. PRATT

The recovery of cæsium and rubidium chlorides from carnallite[1,2] and from plant ashes[3] has been mentioned earlier (see page 2196). Cæsium chloride can be prepared[4] by passing hydrogen chloride gas into a paste of a cæsium salt with its saturated aqueous solution. The chloride can also be recovered from the cæsium mineral pollucite.[5-7] Harned and Schupp[8] made pure samples of the salt from pollucite in the following way. The powdered mineral was dissolved in concentrated hydrochloric acid. The aluminium present in the filtrate was removed as the hydroxide, and the remaining solution was evaporated several times with hydrochloric acid to give a mixture of cæsium chloride with other alkali metal chlorides. The cæsium was precipitated as the double salt with antimony trichloride, which was filtered off and hydrolysed to give an acid solution of the chloride. Excess antimony was precipitated as the sulphide and the solution evaporated to dryness. The salt was purified by adding iodine to its aqueous solution, followed by chlorine gas. The precipitated $CsICl_2$ was recrystallised and decomposed by heat to give a sample of cæsium chloride containing about 0·1% of impurity.

Cæsium and rubidium chlorides can be separated by fractional precipitation of part of the rubidium with ethanolic hydrogen chloride,[1,9] followed by the precipitation of cæsium as the double salt with antimony trichloride. The double salt, which can be purified further by recrystallisation from hydrochloric acid,[7] loses the antimony trichloride when heated for one or two hours in a vacuum at 450°C.[7] It is claimed that a better purification results from forming the double salt $CsHgCl_3$ by treating the chloride (15 g.) with mercuric chloride (20 g.) in hot hydrochloric acid.[10] The precipitate so obtained is recrystallised and decomposed by heat.

Cæsium chloride can be separated from large amounts of sodium chloride by precipitating the latter by passing hydrogen chloride into a solution of the mixed salts in strong hydrochloric acid. The filtrate, which is considerably enriched in cæsium, is evaporated and the solid dissolved in ethanolic hydrochloric acid, from which the remaining sodium chloride is precipitated by passing more hydrogen chloride.[11]

Barrer and Sammon[12] found that an ion sieve reagent, silver analcite, can be used to separate cæsium from other alkali metal chlorides. The removal of sodium and potassium is complete, the separation from sodium being good enough to be used in quantitative analysis, though with potassium a little cæsium is retained by the sieve. The conditions are more critical for the separation of rubidium from cæsium, but complete separation is again possible if methanol or ethanol is used as the solvent. Kayas[13] also achieved complete separation of the alkali metal cations (as chlorides) in Amberlite IR100 ion exchange resin, the sodium and potassium being eluted with 0·1 N. hydrochloric acid and rubidium and cæsium with 1·0 N. acid. Better separations are possible using inorganic exchange reagents, as have been mentioned under rubidium chloride (see page 2196). Some separation of sodium and cæsium is obtained on a clay-asbestos column.[14] Small amounts of alkali chlorides can be separated by paper chromatography.[15,16] Cæsium chloride is much more volatile than potassium and rubidium chlorides at 440°C. in a vacuum,[17] and can thus be separated from them by sublimation.

Pure samples of cæsium chloride were prepared by Baxter and Harrington[18] who determined the atomic weight of caesium by comparing the chloride with silver. Pure caesium nitrate was recrystallised fractionally until the rubidium content was much less than 0·005%. The purest fractions were recrystallised from hot water several times, and a solution of the final crystallised salt was added to perchloric acid to give a precipitate of the perchlorate. This salt was recrystallised three times and heated in platinum vessels to give the chloride. The chloride was recrystallised at low temperatures from hydrochloric acid containing a little hydrazine to prevent the attack on the platinum vessels which otherwise occurred. The recrystallised samples were fused in a stream of dry hydrogen containing 2—30% of dry hydrogen chloride.

Caesium chloride can be analysed for cæsium by the methods of flame photometry[19] and arc emission spectroscopy.[20] Some aspects of the separation and analysis of cæsium chloride have been discussed under rubidium chloride (see page 2197).

Crystalline Caesium Chloride.

Under normal conditions, caesium chloride has the simple body-centred cubic lattice to which it has given its name, in which each ion is surrounded by eight of the opposite kind at the corners of a cube. The length of the cubic unit cell side at 20°C. has been given as 4·1180 ± 0·0005 A.[21] and as 4·113 A.;[22] at 25°C. the value 4·110 A. has been given.[23] The lattice energy was calculated by Huggins[24] to be 153·1 kg.-cal./mole on the basis of the Born—Mayer equation, the value derived from the Born cycle being 153·2 kg.-cal./mole.[25] Krebs[26] states that polarisation forces are negligible in determining the type of lattice formed, and Neugebauer[27] claims that van der Waals forces decide the lattice structure.

The caesium chloride lattice expands on heating: between 20°C. and 469°C., the unit cell dimension a is given by the expression[21]

$$a \times 10^4 = (41180 \pm 4) + (1{\cdot}8197 \pm 0{\cdot}017)(t - 20) + (1{\cdot}00 \pm 0{\cdot}4)(t - 20)^2 \times 10^{-3}$$

where t is the temperature in °C. The molar volumes computed[28] at 25°, 100°, 200°, 300°, 400° and 469°C. are 42·1, 42·6, 43·2, 44·0, 44·8 and 45·4 c.c./mole respectively. The root mean square amplitude of thermal vibration of the cæsium ion is about 10% greater than that of the chloride ion; the values of these two amplitudes at 20°, 150°, 250°, 350°, 400°, 435° and 460°C. are 0·184, 0·218, 0·243, 0·265, 0·285, 0·309 and 0·333 A. respectively for cæsium, and 0·165, 0·203, 0·230, 0·254, 0·268, 0·284 and 0·301 A. respectively for chloride.[21]

Cæsium chloride is the only alkali halide which is known to have a crystalline transition between room temperature and the melting point under normal pressure. At about 470°C. there is a transition to a face-centred cubic lattice of the sodium chloride type. Menary, Ubbelohde and Woodward[21] found, by X-ray diffraction methods, that the transition occurs sharply at 469°C., and at approximately this temperature the unit cell dimension of the high temperature form is 7·042 A. The heat change during the transition is 1·81 kg.-cal./mole and the entropy change is about 2·4 e.u. at 469°C. Wood, Sweeney and Derbes[33] give the unit cell dimension of the high temperature form as $a_t = 7{\cdot}10 + 4{\cdot}2(t - 480) \times 10^{-4}$ A. where t is the temperature in °C. This equation gives approximate values, and they suggest that precise determinations of the distances are required, since there seems to be a sudden rather large increase in the dimension in the region just above the transition point. Johnson, Agron and Bredig,[28] also using X-ray methods, found the transition point at 470°C. They give the values 53·4, 53·6, 54·4 and 54·8 c.c./mole for the molar volumes at 470°, 500°, 600° and 645°C. The authors mentioned above[21,28, 33] discuss the hysteresis in the transition, and the presence of hysteresis is confirmed by the recent work of Wood, Secunda and McBride[29] who found, by the method of differential thermal analysis, that the transition occurs at 465°C. with rising temperature and at 472°C. when the temperature is falling. A marked hysteresis around the transition is also shown by the electrical conductivity of the solid, which drops sharply on passing to the high temperature form.[30]

Menary *et al.*[21] remark that there does not seem to be a satisfactory explanation of this transition. It is unlikely to be determined by the radii of the ions, since the simple criterion for the stability of a body-centred cubic lattice, that the ratio $r+/r-$ should be greater than 0·732, is still satisfied in caesium chloride at 469°C., when the ratio is about 0·915 at the least. They suggest that the progressive development of lattice flaws at high temperatures in the body-centred form may lower the lattice energy sufficiently for the transition to occur. In support of this, they observed that the intensities of some of the *X*-ray reflections from the lattice fade rapidly as the transition temperature is approached, as would be expected if lattice defects were becoming numerous. The effect of added foreign ions in decreasing the heat of transition is quoted as evidence in favour of this interpretation. The fact that the conductivity decreases sharply on going to the high temperature form could also be the result of an increased number of lattice defects in this form.[30] May[31] had earlier made calculations of the lattice energies of the two forms of caesium chloride. In order to account for the increased stability of the low temperature form he found it necessary to allow for the distortion of the ions from spherical symmetry. Buerger[32] has discussed the transition in terms of the crystal structures. The body-centred lattice can easily change into the face-centred form if the cube expands along one trigonal axis and contracts at right angles to this axis. This process alters the number of contacts from 8 to 6 without any intermediate stage being required, and would require only a small energy of activation.

Menary *et al.*[21] state that the transition temperature is insensitive to the presence of other ions in the lattice, a decrease of 1°C. being produced by 1 mole-% of potassium or rubidium chlorides. The effects of foreign ions have been measured by Wood *et al.*[29,33] The transition temperature is raised if the chloride contains cæsium bromide which has a body-centred cubic lattice and is more soluble in the low temperature form of the chloride. The transition temperatures for mixtures containing 20, 40, 50 and 60 mole-% of the bromide are about 482°, 514°, 542° and 578°C. respectively.[29] The values quoted here are approximate since the transitions show hysteresis. Alkali halides with face-centred lattices should be more soluble in the high temperature form of caesium chloride and consequently they should lower the transition temperature. It is lowered by 10–15°C. by the presence of 1 mole-% of potassium chloride,[33] and for samples containing 0, 15, 10, 20 and 50 mole-% of rubidium chloride, the transitions to the face-centred lattice are complete at 472°, 438°, 395°, 355° and 215°C., respectively.[33] At room temperature, up to 30% of cæsium chloride can remain in solid solution with rubidium chloride in a face-centred lattice.

Cæsium chloride also adopts the sodium chloride structure at room temperature when it crystallises in thin layers on the surfaces of other crystals. Schulz[34–36] found that on surfaces of sodium nitrate and calcium carbonate, the sodium chloride lattice of cæsium chloride has a unit cell dimension of 6·94 A.; hence the interatomic distance of 3·47 A. is 0·1 A. smaller than it is in the normal cæsium chloride structure.

Villa[37] has calculated that the free energy of formation for the process

$2Cs(liq.) + Cl_2(gas) \rightarrow 2CsCl(solid)$ over the temperature range 298°–915°K. is given by the equation $\Delta G = -213750 - 6{\cdot}7\,T\log T + 66{\cdot}40\,T$ (±3) where T is the absolute temperature.

For the normal form, the density is given as 3·9905 g./c.c. at 20°C.,[22] as 3·988 ± 0·004 at about 20°C.,[38] and as 3·988 at 25°C.[39] Bridgman[40] found the fractional decrease in volume to be 0·166 for an increase in pressure from 0–50,000 kg./cm.^{2} and 0·067 for an increase from 50,000–100,000 kg./cm.^{2} Szigeti[41] calculated the value $5{\cdot}05 \times 10^{-6}$ cm.^{2}/kg. for the coefficient of compressibility, compared with the experimental value of $5{\cdot}83 \times 10^{-6}$.

The refractive index is 1·6396 at 25°C.[39] and 1·6393 at 26°C.;[42] the values at about 25°C. change from 1·6347 at $\lambda = 6700$ to 1·8226 at $\lambda = 2260$.[43] The chlorine K' valence spectrum ($3p \rightarrow 1s$) can be observed in the second order at about 9 A.[44] The absorption spectrum in the ultra-violet region[45] is said to correspond to the excitation of the caesium ion to an excited state, whilst the chlorine ion remains in a ground state. The magnetic resonance absorption of the ^{133}Cs nucleus in the solid is centred at a magnetic field strength which is 1·63 p.p.m. lower than the value for the saturated aqueous solution.[46] The difference could be a result of partial covalent bonding in the solid. Brindley and Hoare[47] found the diamagnetic susceptibility at about 20°C. to be $56{\cdot}7 \pm 0{\cdot}19 \times 10^{-6}$ c.g.s. units. Schupp[48] found the dielectric constant at 1800 metres wave-length to be 6·34; Skavani[49] has calculated this quantity theoretically. Davisson[50] discusses the process of electrical breakdown in the lattice. Warren and Griffiths[51] have studied the annihilation radiation of positrons decaying in caesium chloride. Measurements are reported on the photoelectric effect[52] and on the positions of the maxima of absorption bonds arising from defects in the lattice.[53,54] The F-centre absorption bands are shifted in position by changes in pressure and temperature.[55]

Molten Caesium Chloride.

The melting point of caesium chloride is 645 ± 2°C.;[56] the entropy of fusion being 3·92 e.u.[28] and the heat of fusion 3·8 kg.-cal./mole.[57] From X-ray diffraction measurements on the solid and liquid near the melting point[28] the molar volume for the liquid at 645°C. is 60·3 c.c./mole. This represents an expansion of only about 10% relative to the molar volume of 54·8 c.c./mole for the solid at this temperature, and it is suggested that the melting process involves mainly the disappearance of the long range order in the crystal, and that each ion in the melt is surrounded by about six others, a situation similar to that in the high temperature form of the crystal. Recently, a more extensive study[58] of the X-ray diffraction patterns of liquid caesium chloride has enabled a radial distribution curve to be drawn. This curve shows two main maxima, one of which represents the closest contacts between Cs^+ Cl^- pairs, each ion having an average of 4·6 neighbours centred at a distance of 3·53 A. Some pairs of ions seem to be as close to each other as about 3·0 A., a distance similar to the internuclear distance in CsCl monomers in the vapour. The second maximum represents the closest contact between ions of like charge, each having an average of about 7·1 neighbours centred at 4·87 A.

The surface tension of caesium chloride is 72 dynes/cm. at 900°C. and 59 dynes/cm. at 1000°C.[59] Yaffe and van Artsdalen[56] found that the specific conductivity in the range 650–900°C., is given by the equation: $\kappa = a + bt - ct^2$ ohm.$^{-1}$cm.$^{-2}$ where $a = -1{\cdot}8023$, $b = 0{\cdot}5628 \times 10^{-2}$ and $c = 1{\cdot}765 \times 10^{-6}$. The standard deviation for κ is 0·003. The density between 670°C. and 905°C. is given by the equation: $\rho = a - bt$ g./c.c., where $a = 3{\cdot}4782$ and $b = 1{\cdot}0650 \times 10^{-3}$, the standard deviation being 0·0006. They calculate that the heat of activation of the conduction process is about 5·7 kg.-cal./mole at 650°C. falling to about 4·8 kg.-cal./mole at 900°C., the corresponding entropy of activation being 6·2 e.u. at 850°C.

Bockris and Richards[60] measured the velocity of ultrasonic vibrations in the liquid salt. Between 660°C. and 1010°C., the velocity is given by the expression $u = 1597 - 0{\cdot}675\,t$ metres/second, where the temperature t is in °C.; the error is ±6 metres/sec. They calculate from their results that at 700°, 800°, 900° and 1000°C., the adiabatic compressibility is 28·7, 33·8, 40·4 and 48·7 × 10^{-12} cm.^{2}dyne,$^{-1}$ and the isothermal compressibility is 42·9, 51·2, 62·7 and 76·3 × 10^{-12} cm.^{2}dyne^{-1} respectively. Also at these temperatures, the cube root of the incompressible volume per ion is 3·17, 3·15, 3·12 and 3·09 cm., the ratio of the specific heats is 1·50, 1·53, 1·55 and 1·57, and the specific heat at constant volume is 10·3, 10·1, 10·0 and 9·9 g.-cal./mole, the specific heat at constant pressure being taken as about 15·5 g.-cal./mole. They discuss the results for all the liquid alkali halides in terms of a structural model of ionic liquids.

Liquid caesium chloride is completely miscible with caesium metal.[61]

Caesium Chloride Vapour.

Treadwell and Werner[17] studied the sublimation of caesium chloride from mixtures with potassium and/or rubidium chloride. At 440°C. in a vacuum, the caesium chloride sublimes one hundred times faster than the other two, and can easily be separated from them in this way. At 600°C., small samples of caesium chloride were found[62] to lose weight at the rate of 0·35, 0·64 and 1·08% per hr. in streams of air, hydrogen chloride and water vapour respectively.[63] The heat of sublimation is given as 44·1 kg.-cal./mole at ~600°C. by Treadwell and Werner[57] and 47·8 ± 0·9 kg.-cal./mole at 0°K. by Niwa.[64] Reis[65] calculated 50 kg.-cal./mole for this quantity.

For the change of vapour pressure with temperature, Cogin and Kimball[66] give $\log_{10}p_{(\mathrm{mmHg})} = 11{\cdot}076 - 11{,}346/T + \tfrac{5}{2} \times \log(1000/T)$, and Treadwell and Werner[57] give $\log_{10}p_{(\mathrm{mmHg})} = -9970/T + 9{\cdot}942$; in both cases the temperature T is in °K. Rice and Klemperer[67] calculated the values of thermodynamic functions shown in Table I.

TABLE I.- THERMODYNAMIC FUNCTIONS FOR GASEOUS CAESIUM CHLORIDE.

Function	Temperature, °K.							
	298·16	400	600	800	1000	1250	1500	2000
$-\frac{G_0-H_0^{\circ}}{RT}$	26·702	27·919	29·641	30·887	31·864	32·850	33·666	34·961
$\frac{S^{\circ}}{R}$	30·793	32·107	33·940	35·247	36·272	37·294	38·142	39·486
$\frac{H^{\circ}-H_0^{\circ}}{RT}$	4·091	4·188	4·299	4·360	4·407	4·445	4·476	4·525

They give 23·9 ± 1·2 g.-cal.-deg.$^{-1}$mole^{-1} for the experimental value of the entropy of the crystal at 298·16°K., compared with the calculated value of 22·0 ± 0·5. Cogin and Kimball[66] give 46·69 ± 0·26 kg.-cal./mole for the heat content at 800°K.

Ionov analysed, by means of a mass spectrometer, the ions produced by electron impact on caesium chloride and other alkali halides in the vapour state, and suggested that these salts existed partly as dimers.[68] Miller and Kusch[69] were unable to detect any effects due to dimers on the velocity distribution in a beam of caesium chloride molecules, and Rice and Klemperer[70] could not find any infra-red absorption lines from dimeric molecules, but Berkowitz and Chupka,[71] who have recently extended Ionov's work, found that the ratio of dimers to monomers in the vapour at about 1000°C. is 0·071 to 1.

Luce and Trishka[72,73] found the interatomic distance in $^{133}Cs^{35}Cl$ to be $r_0 = 2{\cdot}88 \pm 0{\cdot}03$ A. by the molecular beam electric resonance method. A later determination by microwave spectroscopy[74] gives $r_e = 2{\cdot}9062 \pm 0{\cdot}0001$ A. The electric dipole moment of $^{133}Cs^{35}Cl$ is 10·46 ± 0·14 debye,[73] and later Trishka derived a more accurate expression $\mu\nu = (10{\cdot}42 \pm 0{\cdot}02) + (0{\cdot}056 \pm 0{\cdot}002)\nu$debye for the dipole moment $\mu\nu$ in the vibrational state characterised by the vibrational quantum number ν.[75] On the basis of a simple electrostatic model, Rittner calculated[76] a value of 10·39 debye for the dipole moment, and Altshuller[77] calculated $1{\cdot}2 \times 10^{-4}$ debye for the difference between the dipole moments of $Cs^{35}Cl$ and $Cs^{37}Cl$, the latter possessing the larger moment.

Rice and Klemperer[70] measured the fundamental vibration frequency of the caesium chloride molecule; it is 209 ± 6cm.$^{-1}$ A low pressure discharge in the vapour produces the ions Cs^-, $CsCl^-$, $CsCl_2^-$, Cs^+, $CsCl^+$ and Cs_2Cl^+.[78,79] Large yields of chloride ion are produced by the decomposition of beams of caesium chloride on a heated tungsten filament.[80] The salt can also ionise in flames.[81] The energy of dissociation into ions in the gaseous state is given as 105kg.-cal./mole.[82]

Aqueous Solutions of Cæsium Chloride

Lange and Martin[83] determined the integral heat of solution at 25°C. as −4·166kg.-cal./mole in water and −4·82kg.-cal./mole in deuterium oxide. The total heat of hydration at 25°C. has been given as 143kg.-cal./mole;[84] the calculated sum of the free energies of hydration of the two ions being 139·8 kg.-cal./mole.[85] The hydration of the ions has been studied by ultrasonic methods.[86] The specific heats of solutions of normality N. at 20°C. are given by $C_p = 0{\cdot}9992 - 0{\cdot}187$ N.[87] Gehlen and Dieter[88] calculated that the solubility at 18°C. should decrease from 65·75wt.-% under normal pressure to 51·6wt.-% under a pressure of 10,000atm. At 25°C., the densities of solutions containing 0·5602, 1·000, 2·269, 2·997, 3·998, 5·001 and 5·998moles/litre are 1·0610, 1·1243, 1·2827, 1·3733, 1·4966, 1·6197 and 1·7408g./c.c. respectively.[89] The apparent volume of the Cs^+ion in solution at 35°C. is given[90] as 21·7c.c./equivalent, and that of the Cl^- ion as 18·1c.c./equivalent. The water vapour pressure over the saturated solution is given by $\log p_{mm.} = -2198{\cdot}5/T + 8{\cdot}5621$.[91] Isopiestic measurements have been reported on solutions of cæsium chloride containing potassium or lithium chlorides[92] or sodium chloride.[93] From the latter measurements Robinson determined the activity coefficients for strong solutions at 25°C. The values are 0·496 at a molality of 2·0; 0·485 at 2·5, 0·479 at 3·0, 0·475 at 3·5, 0·474 at 4 and at 4·5, 0·475 at 5·0, 0·480 at 6·0, 0·486 at 7·0, 0·496 at 8·0, 0·503 at 9·0, 0·508 at 10·0, and 0·512 at 11·0molal. For more dilute solutions at 25°C., Robinson and Stokes[94] give 0·495 at 2·0 *m.*, 0·501 at 1·8, 0·509 at 1·6, 0·518 at 1·4, 0·529 at 1·2, 0·544 at 1·0 *m.*; 0·553 at 0·9 *m.*, 0·563 at 0·8, 0·575 at 0·7, 0·589 at 0·6, 0·606 at 0·5, 0·628 at 0·4, 0·656 at 0·3, 0·694 at 0·2 and 0·756 at 0·1 *m.* For very dilute solutions, Harned[95] gives the values of the activity coefficient at 25°C. as 0·899, 0·927, 0·951, 0·965 and 0·975 for solutions containing 10, 5, 2, 1 and 0·5millimoles/litre respectively. These values are based on measurements[96,97] of the diffusion coefficient at 25°C., which varies from $1{\cdot}946 \times 10^{-5}$ at 0·01287 *m.* to $2{\cdot}007 \times 10^{-5}$ at 0·00122 *m.*, the limiting value at infinite dilution being $2{\cdot}046 \times 10^{-5}$. The "isoactive" concentration, at which the activity coefficient of water in the solutions is equal to that of pure water,[98] is 4·9 *m.*[99] The thermodynamic properties of the solutions in the range 0·1 to 2·0M. can be interpreted satisfactorily[100] if allowance is made for the lack of interpenetration of the hydration spheres of similarly charged ions, and for ion pair formation between oppositely charged ions. The dissociation constant of the Cs^+Cl^- ion pair in solution at 25°C. has been determined to be $2{\cdot}8_5$ from data on activity coefficients,[101] compared with an earlier value[102] of 3·2 derived from conductivity measurements.

The differences ($n_s - n_0$) between the refractive indices of the solution (n_s) and that of water (given as $n_0 = 1{\cdot}333151$) at 18°C. were found to be $25{\cdot}6 \times 10^{-6}$ at 0·002 N., $22{\cdot}5 \times 10^{-6}$ at 0·0016 N., $19{\cdot}8 \times 10^{-6}$ at 0·0013 N., $15{\cdot}6 \times 10^{-6}$ at 0·001 N., $13{\cdot}5 \times 10^{-6}$ at 0·0008 N., and $6{\cdot}9 \times 10^{-6}$ at 0·0004 N.[103] The concentration dependence of the equivalent refractivity has been considered theoretically.[104,105] The dielectric constants[106,107] and magneto-optical rotations[108,109] of the solutions have been measured; at 0°C., the molecular magneto-optic rotations are 7·45°, 7·03° and 6·51°C. for solutions containing respectively 59·6, 39·3 and 14·1% of the salt.[110] The conductivity of the solutions has been discussed theoretically;[111-113] the equivalent conductivity passes through a maximum value with increasing pressure.[114] In supercritical water, cæsium chloride behaves similarly to sodium chloride.[115] The electrolysis of cæsium chloride solutions is expected to produce better yields of alkali than are obtained from potassium chloride,[116] since the transference number of the cation should be larger for caesium in the presence of hydroxide ions.

Non-aqueous Solutions of Cæsium Chloride

At 18°C., the equivalent conductivity of cæsium chloride in solution in hydrogen cyanide is given by the equation $\Lambda_c = 368{\cdot}2 - 200\sqrt{c}$ where c is the concentration in moles/litre; the determinations were made on solutions up to 0·002 N. in strength.[117] The solubility in liquid sulphur dioxide at 25 ± 0·02°C. is 0·294 g./100 g. of solution.[118] In anhydrous phosphorus oxychloride,[119] the solubility at 20°C. is 1·26 g./litre, and the specific conductivity of the saturated solution is $1{\cdot}1 \times 10^{-4}$ ohm^{-1}. In methanol at 18°C., the solubility is 3·39 g./100 g. of saturated solution, equivalent to 0·158 moles/litre, and the density of this solution is 0·810 g./c.c.; in methanol at 25°C., the corresponding values are $L^{25} = 3{\cdot}01$ g./100 g.; $C^{25} = 0{\cdot}141$ moles/litre and $d^{25} = 0{\cdot}83$ g./c.c.[120] For the solutions in acetonitrile, $L^{18} = 8{\cdot}3 \times 10^{-3}$, $C^{18} = 3{\cdot}9 \times 10^{-4}$ and $d^{18} = 0{\cdot}783$; and $L^{25} = 8{\cdot}4 \times 10^{-3}$, $C^{25} = 3{\cdot}9 \times 10^{-4}$ and $d^{25} = 0{\cdot}777$. For solutions in formic acid, $L^{18} = 107{\cdot}7$, $C^{18} = 5{\cdot}82$ and $d^{18} = 1{\cdot}896$; $L^{25} = 130{\cdot}5$, $C^{25} = 6{\cdot}68$, and $d^{25} = 1{\cdot}987$. The activity coefficients of 0·02, 0·1 and 0·4 molal solutions in formamide are 0·922, 0·858 and 0·797 respectively.[121] The minimum value of $\Delta t/m$, where Δt is the depression of freezing point, is at $m = 0{\cdot}4$. Caesium chloride dissolves in benzene solutions of aluminium tribromide,[122,123] and a dipole moment of 10·9 debye is given for the species $CsCl,Al_2Br_6$.[123,124] At 20°C., the molar solubility in concentrated hydrochloric acid is 4·725, and in ethanol it is $0{\cdot}29 \times 10^{-2}$.[11]

Mixed Crystals Containing Cæsium Chloride

Caesium chloride, which when liquid is completely miscible with liquid caesium metal,[61] is soluble as a solid in the liquid metal to the extent of about 15—25 mole-%. The partial heat of solution is 22 ± 2 kg.-cal./mole. The cæsium chloride which solidifies from the molten mixtures contains a little cæsium in solid solution, giving the solid a deep purple blue-black colour.

Some properties of the solid solutions with other alkali halides have been mentioned in the discussion of the phase transition (see page 2355). A solid solution is formed with caesium bromide, and measurements of the X-ray diffraction patterns[29] and refractive indices[42] of the solids show that the solutions are formed even when the powdered components are mixed and heated below the melting point at 400°C. The refractive index of the 50/50 mixture at about 28°C. is 1·665.[42] The melting points in the system with rubidium chloride change smoothly with concentration.[33] With potassium bromide, an equilibrium mixture is produced by heating the salts together, (even below the melting point), according to the equation $CsCl + KBr \rightleftharpoons CsBr + KCl$.[125] The equilibrium is complete after heating for 3 days at 477°C.; the equilibrium mixture is a mixture

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of the two binary common-ion solid solutions, CsBr/CsCl and KBr/KCl.

Magnesium chloride gives three compounds, $CsCl,MgCl_2$, $2CsCl,MgCl_2$ and $3CsCl,MgCl_2$, and a congruent melting point is found at the composition $CsCl{:}3MgCl_2$.[126] With calcium chloride, there are two eutectics at 10 mole-% CsCl (708°C.) and 90·5 mole-% CsCl (610°C.), and a compound $CsCaCl_3$, which melts at 1030°C., is formed.[127] This compound is isomorphous with $RbCaCl_3$. Chu and Egan,[128] who give a reproduction of the phase diagram of this system, have calculated the free energies of the components, and other thermodynamic properties, and show that the system shows large negative deviations from ideal behaviour. With strontium chloride, the compound $CsSrCl_3$ (m.p. 907°C.) is formed,[127] and with cadmium chloride,[129] the compounds $CsCdCl_3$ (m.p. 545°C.) and Cs_2CdCl_4 (m.p. 462°C.).

The systems $RbCl{-}CsCl{-}CaCl_2$[127] and $RbCl{-}CsCl{-}CdCl_2$[129] have also been studied. In the system $CsCl{-}LiCl{-}H_2O$ the double salt $2CsCl,LiCl,4H_2O$ is stable at 25°C. and 40°C.[130] The system KCl–RbCl–CsCl has been recorded[131] but both the melting point and transition temperature given for caesium chloride are low. Caesium chloride and silver chloride form a peritectic system,[132] whereas a simple eutectic system is found with silver iodide.[133] Caesium chloride crystals containing thallous chloride behave as phosphors.[134, 135]

A simple eutectic is formed with caesium vanadate;[136] there are several eutectics with lithium sulphate[137] and a eutectic occurs with potassium sulphate.[138] The surface tension of molten lithium sulphate is markedly decreased by the addition of small amounts of caesium chloride.[139] A small proportion of caesium chloride stabilises the cubic phase of ammonium nitrate.[140]

Miscellaneous Reactions

The bombardment of caesium chloride by high energy protons gives radioactive isotopes of barium.[141] Wartenberg[142] studied the effect of caesium chloride in producing a noticeable attack of platinum by hydrochloric acid solutions, a reaction which had earlier been noted by Baxter and Harrington.[18] (see also page 2354). In 1 hr. at 105°C., a solution of 2 g. of caesium chloride in 100 c.c. of 10% hydrochloric acid had produced 1 mg. of $PtCl_6^{=}$ from the metal. As with potassium chloride, the insolubility of the alkali chloroplatinate displaces the equilibrium $Pt + HCl \rightleftharpoons PtCl_6^{=}$ to the right hand side.[142] Similarly, considerable quantities of chloroplatinate are produced from platinum by molten caesium chloride in the presence of hydrogen chloride.

West prepared the compound $Cs^+HCl_2^-$ by the reaction between hydrogen chloride and a concentrated aqueous solution of caesium chloride.[143] The presence of small amounts of the HCl_2^- ion with caesium had earlier been suggested by the behaviour of molten caesium chloride with hydrogen chloride.[144] Double chlorides of other metals with caesium are often relatively insoluble and show characteristic crystalline forms; Ducloux[145, 146] has reviewed their application in microchemistry. With thallic chloride several complex chloride salts, such as $Cs_3[TlCl_6]$, are obtained.[147] Caesium chloride is reduced by lithium hydride to give caesium metal and hydrogen,[148] and reacts with gaseous vanadium tetrachloride to give an unstable complex chloride.[149] It is converted completely to the borate by heating for 10 min. at 400°C. with 8 parts of boric acid,[150] and is an effective catalyst for nucleation during the condensation of sodium crystals from the vapour.[151]

The chloride is more effective than other alkali metal chlorides in coagulating sols of arsenic sulphide[152] or graphitic oxide,[153] and more effective than potassium chloride in producing a complete disorientation of collagen fibres.[154] Lyding[155] disproved an earlier claim that 90% of the infectious diseases in mice could be cured by administering caesium chloride.

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SECTION LXXXVIII

CAESIUM BROMIDE

By N. R. W. BENWELL

Preparation

Cæsium bromide is separated from mixtures of bromides of the alkali metals by treatment with liquid bromine which dissolves the cæsium bromide leaving substantially undissolved all other alkali halides. Cæsium bromide is recovered by evaporation of the separated liquid bromine solution.[1] The method, slightly modified,[2] is used for the recovery of cæsium bromide from ores such as pollucite, $H_2Cs_4Al_4(SiO_3)_9$. The powdered ore is dissolved in 30% excess of hydrobromic acid, filtered, concentrated and the alkali metal bromides precipitated with *iso*propyl alcohol. Cæsium bromide is dissolved from the dried precipitate by extraction with about 10 parts of liquid bromine per part of Cs_2O in the ore and is then recovered by evaporation.

Cæsium bromide is also recovered from pollucite by treating the ore with aqueous hydrobromic acid and the resulting solution with a hydrobromic acid solution of antimony tribromide to form $3CsBr,2SbBr_3$ which, on heating in vacuo, loses antimony tribromide and leaves pure cæsium bromide.[3]

Physical properties

The nature of the lattice structure of the alkali halides is determined by the importance of the van der Waals forces. Cæsium bromide is strongly polarizable and has a CsCl–type lattice.[4]

However, in considering the effect of the eigenfunctions of the outer electrons in ions (directional forces) on the type of lattice formed, the polarization forces are said to be negligible for univalent ions of large size such as in caesium bromide.[5]

X-Ray diffraction patterns of caesium bromide taken up to the melting point give no evidence of any transition from simple cubic to face-centred cubic structure similar to the transition which occurs in cæsium chloride at 469°C. Consideration of the molar volumes of the solid and molten salts at the melting points leads to the conclusion[6] that the structural alteration from 8- to 6-fold co-ordination, which in cæsium chloride takes place in the solid phase at 469°C., occurs in the case of cæsium bromide at the m.p. as part of the fusion process. The volume expansion on melting for cæsium bromide of 26·5% is essentially equal to the sum of the expansions for cæsium chloride at the transition and melting points, 17·1 + 10·0 = 27·1%.

When an aqueous solution of cæsium bromide is evaporated slowly the rhombic dodecahedral form (110) is obtained, while at higher rates of evaporation the cubic form (100) is obtained. For low rates of evaporation (low degree of supersaturation) planes with low electric fields, *i.e.* planes containing both cations and anions, form the faces (100) for NaCl–type and (110) for cæsium chloride type lattices. For high rates of evaporation, planes consisting of either cations or anions alone form faces (111) for

NaCl–type and (100) for the CsCl–type lattices.[7]

When cæsium bromide (CsCl–type) is deposited by evaporation on the cleavage surface of mica, lithium fluoride, sodium chloride, potassium bromide, potassium iodide and calcium carbonate, electron diffraction examination has shown that in all cases the crystals touching the substrate have the NaCl–type structure. The lattice parameter a_0 for the new structure is 7·23 A. and the interatomic distances are lower than in the CsCl–type structure.[8] In the examination of thin overgrowths by multiple scattering of electrons,[9] the electron beam reflected from the substrate is useful as the incident beam on an oriented overgrowth such as cæsium bromide deposited by evaporation in a vacuum on a single crystal of lithium fluoride to a thickness of 2 A.

Long exposure to 'intense *X*-rays' in a light tight box produces colouration in cæsium bromide crystals. The colour fades logarithmically with exposure to daylight, and fading may also be induced by radiation from a 500-watt lamp.[10]

The orientations of cæsium bromide and other alkali halide crystals grown from the vapour and from solution on the cleavage faces of calcium carbonate and sodium nitrate have been determined by electron diffraction. A deposit 10 A. in thickness showed a well defined pattern in most cases but with thicknesses greater than 150 A. random orientations occurred. Factors of importance in controlling orientation are (1) low index planes lie parallel to the substrate surface, (2) the contact planes usually contain ions of both signs, (3) dimensions along rows of like ions must match. Growths from vapour and from solution do not always show the same orientation or even the same crystal structure.[11]

The frequencies and anharmonicities of the lattice oscillations of cæsium bromide, *i.e.* the oscillations of the interpenetrating lattice of the caesium and bromine ions with respect to one another, have been calculated on the basis of the Born model. The calculated value of the frequency of lattice oscillation, $2{\cdot}1 \times 10^{-12}$, is in good agreement with the observed value of $2{\cdot}2 \times 10^{-12}$ (Barnes). The anharmonicity of the lattice oscillation, unlike its frequency, varies with the direction of the oscillation, from a large positive value along [111] to a small negative value along [100].[12]

Preparations of cæsium bromide by different thermal treatments differ slightly from each other in their heats of solution and in the presence of 'excessive' weak lines in their *X*-ray photographs with a period double or quadruple the basic lattice period. The varying values of the heat of solution are attributed to differences in the crystallographic lattice of the salt.[13,14]

The following physical properties[15] have been determined to evaluate the use of cæsium bromide in optical instruments:

Young's modulus	= $1{\cdot}6 \times 10^{11}$ dynes/cm.^{2}
Apparent elastic limit	= $8{\cdot}4 \times 10^{7}$ dynes/cm.^{2}
Modulus of rupture	= 16·5 dynes/cm.^{2}
Total inelastic deformation in 50 hr.	= $1{\cdot}65 \times 10^{-3}$ cm.
Steady-state rate of cold flow	= $12{\cdot}5 \times 10^{-6}$ cm. hr.$^{-1}$
Knoop hardness number (for 200 g. load)	= 19·5
Thermal conductivity	= 22×10^{-4} g.-cal. sec.$^{-1}$ cm.$^{-1}$ °C.$^{-1}$
Short wave-length limit mμ (for 10 mm. thickness)	= 205
Long wave-length limit μ (for 42 mm. thickness)	= 40
Melting point	= 636°C.
Solubility	= 124·3 g. per 100 g. of water

The cubic compressibility of cæsium bromide is given as 7·0 per megabar × 10^{-6} as derived from the semi-empirical equation:

$$\beta = kV_m/U$$

where β = compressibility; k = empirical constant; V_m = molecular volume; U = molecular heat of formation of the salt.[16]

The compressions of cæsium bromide under 50,000 kg./sq.cm. at room temperature and at the temperature of solid carbon dioxide are given as 0·1748 and 0·1689 respectively.[17] Other determinations by the same author[18] give the compression or volume decrement of cæsium bromide as 0·186 for 0–50,000 kg./sq.cm. and 0·086 for 50,000–100,000 kg./sq.cm.

The following relation has been derived[19] between the compressibility and absorption frequency of ionic crystals.

$$\frac{1}{\kappa} = \frac{R^2}{3U} \cdot \frac{\epsilon + 2}{n^2 + 2} \cdot m\omega_t^2$$

κ = compressibility, ω_t = absorption frequency, R = nearest neighbour distance, U = volume occupied by an ion pair, ϵ = static dielectric constant, m = reduced mass of ion pair, $1/m = 1/m_1 + 1/m_2$, n = optical refractive index. For cæsium bromide κ (calculated) = 6·0 × 10^{-6}cm.^{2}/kg. κ (observed) = 6·92 × 10^{-6}cm.^{2}/kg. Ratio κ_c/κ_0 = 0·87.

A fair agreement with that obtained from experimental data is found[20] when the thermal expansion of cæsium bromide is calculated from Frenkel's expression for ionic crystals:

$$a = [(n + 4)/2(n - 1)][c/\omega_k]$$

where n = exponent in the expression which characterises the energy of the repulsive forces; c = heat capacity per g.-atom; ω_k = coulomb portion of the energy of the ionic crystals as calculated by Madelung.

Calculations[21] of the dielectric constant of cæsium bromide by various methods differing in the evaluation of the ionic polarizability give values in satisfactory agreement with experimental data. The evaluation is based on the calculation of an elastic force coefficient k between opposed ions as the second derivative of the repulsion energy from formulæ of the type:

$$k = 1{\cdot}16(n - 1)q^2/r_0^3$$

where n = exponent of repulsive energy law; q = charge of the ion; r_0 = nearest distance in the lattice.

The heat of vaporisation of cæsium bromide has been determined[22] from the expression

$$\lambda = -1{\cdot}985 \times 2{\cdot}303 \times [\mathrm{d}\log p/\mathrm{d}(\tfrac{1}{T})]$$

to be 36,870 g.-cal. The same author gives the boiling point as 1297°C. by calculation or extrapolation of vapour pressure data, and a critical temperature of 2433°K. Greater accuracy is claimed for these results than for those calculated by the Ramsay-Young Rule. For gaseous cæsium bromide, the interatomic distance = 3·17 A. the fundamental frequency = 192 cm.$^{-1}$ and the entropy ($S_{298{\cdot}1}$) = 61·5 g.-cal./deg., the uncertainty being ± 0·3 e.u.[23] Vapour pressure data measured between pressures of 0·001 and 0·1 mm. by means of a diffusion method using an oxide-coated tungsten filament as detector[24] fit the equation:

$$\log p_{\mathrm{mm.}} = c - A(1000/T) + {}^5\!/_2\log(1000/T)$$

Values of A and C for cæsium bromide are 11·421 and 11·676 respectively.

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Heat content (heat of vaporization) at 800°K. = 48·26 ± 0·33 kg.-cal./mole. Entropy of vaporization at 800°K. = 60·35 g.-cal./degree. The vapour pressure curves of the alkali bromides at temperatures between the boiling point and 200–300°C. below the boiling point of the salt lie closer than those of the fluoride and chloride but are more widely separated than those of the iodides.[25]

By directing a molecular beam of cæsium bromide at a thoriated tungsten wire (at 1200–1500°K.) large yields of bromine negative ions have been obtained.[26] The maximum and stable yields were 20% and 11% respectively. These yields are more than for cæsium iodide and fluoride but less than for cæsium chloride.

Ramsay has shown that chemical shifts result from precessional motions induced by the applied magnetic field in the electrons surrounding the nucleus. This precessional motion produces a small local field at the nucleus in opposition to the applied field and this local field will vary from molecule to molecule as a result of the variations in electronic structure. 100% ionic compounds have no chemical shifts and so the shielding change observed for cæsium iodide indicates that there is some covalent character in the crystalline bond.[27] The chemical shift of the ^{133}Cs magnetic resonance,

$$\Delta\sigma = (H_s - H_r)/H_r \times 10^4$$

where H_s and H_r are the magnetic fields necessary for resonance at a fixed frequency for the sample and reference respectively, is −2·08 for cæsium bromide, the reference being a saturated aqueous solution of cæsium chloride. The magnetic shielding of the alkali metals decreases from the fluoride to the iodide while the ion in solution has the largest shielding of all. The larger shifts of cæsium support the observation that chemical shifts increase with the nuclear charge.

The addition of cæsium bromide to the SO_2–$SOBr_2$ system strongly catalyses the exchange at 0°C. The catalysis is homogeneous with exchange rates apparently of first order as to catalyst concentration and zero order as to $SOBr_2$ concentration. The reaction is interpreted as involving basic catalysis by bromide ions. The value of k for cæsium bromide, based on the expression, rate = k (catalyst concentration) is roughly comparable with that of tetramethylammonium bromide *viz.* $6{\cdot}2 \times 10^{-3}$/min. at 0°C.[28]

If an equimolecular mixture of cæsium chloride and potassium bromide or cæsium bromide and potassium chloride is heated for three days at 477°C. *i.e.* below the melting point, an equilibrium is attained as represented by $CsCl + KBr \rightleftharpoons CsBr + KCl$. If either CsCl or KBr is added to the mixture before heating, the equilibrium moves to the right and if CsBr or KCl is added, the equilibrium moves to the left. These changes are in quantitative agreement with the law of mass action. The results at 400°C. are also in accord with the law although the quantitative agreement is not as close as at the higher temperature.[29]

In investigating solid solution mixtures of cæsium bromide and chloride measurement of refractive index has been suggested to supplement *X*-ray crystal analysis. The lines of a series of similar *X*-ray patterns such as are frequently formed by a continuous series of solid solutions may overlap and form a pattern apparently of one compound but having wide lines. The spacings obtained are then average values and the mixture appears homogeneous. Measurements of refractive index, n, by the immersion method are then suggested, since examination of individual particles makes it possible to distinguish between particles of solid solutions of different compositions.[30]

When the silver halides are combined with their corresponding alkali halides, the phase diagrams show certain regularities. With the chlorides, lithium and sodium form solid solutions, potassium and rubidium form eutectics, and cæsium forms a peritectic; with the bromides, lithium and sodium form solid solutions, potassium forms a eutectic and rubidium and cæsium peritectics; and with the iodides only lithium forms a solid solution, sodium a eutectic and potassium, rubidium and cæsium peritectics. The change from one type of diagram to the other is attributed to the formation of complexes.[31]

The variation, with pressure, of the solubility of cæsium bromide in water at 25°C. is as follows:

Pressure (bars)	Solubility (g./100 g. H_2O)
1	123·7
505	117·9
1010	111·9
1510	106·8

The author[32] gives the compressibility of the solid solute (cæsium bromide) at atmospheric pressure as 71 reciprocal bars × 10^{-7}.

The influence of the salt concentration on the compression of an aqueous solution of cæsium bromide is given[33] by an equation expressing the apparent compression as a linear function of the square root of the volume concentration, *viz.*:

$$\frac{A}{r_2} = a + bc^{1/2}$$

where A/r_2 = apparent compression; $r_2 = x_2/x_1$ where x_2 = weight fraction of salt in solution, x_1 = weight fraction of water in solution; c = volume concentration in g. per c.c. at 25°C. and 1 bar pressure; and for cæsium bromide $a \times 10^4 = 84$, $-b \times 10^4 = 59$. Calculations are valid over a pressure range of 1 to 1000 bars at 25°C. and are in good agreement with values obtained from the equation:

$$A = -\Delta p V_w + \Delta p V / x_1$$

where $-\Delta p V_w$ = specific compression of water and $\Delta p V$ = specific compression of solution. The effects of salts on the compression of water increase with the charge on the solute ions and decrease with ionic radius, but there is some other unidentified effective factor.

The supersaturation limits for cæsium bromide in aqueous solution are calculated from the formula:

$$T_s - T = 13\sigma V_{\mathrm{M}} / \lambda$$

where T_s = absolute saturation temperature; T = absolute temperature of first spontaneous crystallization; σ = specific surface energy; V_{M} = molecular volume; λ = heat of solution. Experimental values given are: $\lambda = 5960$; $\sigma = 138$; $\sigma V_{\mathrm{M}} = 6979$, giving $T_s - T = 15{\cdot}2$°C., but no great accuracy is claimed for these results. The radius of the stable crystal nucleus at the first temperature of spontaneous crystallization is shown to be of the order of 10^{-6}cm. and varies hyperbolically with the degree of supersaturation.[34]

The equation:

$$(V_2^x - V_2^i) = -\frac{Nq^2}{2a} \cdot \frac{1}{\kappa^2} \cdot \frac{\mathrm{d}\kappa}{\mathrm{d}P}$$

has been used to determine the apparent expansion coefficient of cæsium bromide in water and in ethylene glycol. (($V_2^x - V_2^i$) = contraction when one mole of salt is dissolved to infinite dilution; q = valence of the ions; a = mean ionic radius; κ = dielectric constant). Simple electrostatic consideration indicates that the change of volume at infinite dilution produced by monovalent salts should be inversely proportional to the mean ionic radii, but while this is true for monovalent bromides in ethylene glycol, it is not true in water. For caesium bromide, contraction in water = 5·6 ml. per mole; contraction in ethylene glycol = 5·2 ml./mole.[35]

Attempts have been made to correlate the solubility of caesium bromide with the dielectric constant of the solvent in the case of water, acetone and a number of alcohols, but because of the many factors involved no general rule has been established.[36]

The total heat of hydration $H^{\pm}$ of caesium bromide has been selected on the basis of measurements of heats of solution at infinite or very high dilution and values of lattice energy U, although the latter term involves an uncertainty of thermodynamic definition. The value given for caesium bromide is 136 kg.-cal./mole. As a principle for the separation of $H^{\pm}$ into heats of solvation H^{+} and H^{-} of the individual ions, Mishchenko rejects assumptions made by Bernal, Fowler and others of approximately equal values of H for ions of equal ionic radii, mainly on account of the dissymmetry of the location of the dipole moment in the H_2O molecule which is estimated to be about 0·25 A. On this basis, heats of solvation for Cs^{+} and Br^{-} become 63 and 72 kg.-cal./g.-ion respectively. Co-ordination numbers, n, (number of H_2O molecules surrounding the ion in the nearest solvate envelope) are for Cs^{+}, 8 and Br^{-}, 8 and are evaluated from the known radii of the ions and the radius r_w of the H_2O molecule. Reasonable values are obtained with $r_w = 1{\cdot}93$ A. corresponding to liquid H_2O but not with $r_w = 1{\cdot}38$ A., the radius of H_2O in ice. The values are at considerable variance with those of Bernal, Fowler and others who attribute $n = 4$ to all univalent ions, on the assumption of a 'frozen' hydrate envelope. The ratio of the heat of solvation H and the co-ordination number n gives the heats of interaction H_1 between the ion and one molecule of H_2O in the solvate envelope as 7·9 kg.-cal./g.-ion for Cs^{+} and 9·0 kg.-cal./g.-ion for Br^{-}. These values can be represented as functions of the ionic radii in the form: $\log H_1^{-} = (1{\cdot}38/r^{-}) + 0{\cdot}25$; $\log H_1^{+} = (0{\cdot}70/r^{+}) + 0{\cdot}47$ and $(1/H_1^{-}) = 0{\cdot}1r^{-} - 0{\cdot}085$; $(1/H^{+}) = 0{\cdot}1r^{+} - 0{\cdot}035$. Simple consideration of electrostatic interaction gives per mol. H_2O an energy of $127{\cdot}06 \times 10^{-16}/(r_i + r_w \pm \beta)^2$ kg.-cal./g.-ion. Values calculated with this formula are in very fair agreement with the experimental values of H_1 for Cs^{+} and Br^{-}, with $\beta = 0{\cdot}25$ and $r_w = 1{\cdot}93$ A. The effective radii of water molecules in the hydrate envelope of Cs^{+} and Br^{-} have been calculated to be 2·10 A. and 2·05 A. respectively, which, being greater than 1·93, indicate an expansion of the hydrate envelope.[37]

From standard electrode potentials of bromine and caesium and from relevant standard free energy data, Kanevskii[38] has calculated a value of 132·9 kg.-cal./mol.$^{-1}$ for the standard free energy of hydration of the pair of ions Cs^{+} and Br^{-}. Wicke and Eigen[39] have introduced two modifications of the Debye–Hückel theory in considering the thermodynamic properties of caesium bromide solution in the concentration range 0·1–2 M.: (1) the hydration spheres of similarly charged ions do not interpenetrate, (2) oppositely charged ions form ion pairs, setting up a dissociation equilibrium, and the authors have found that the concentration dependence of the activity coefficients, heats of dilution, apparent molar heat capacities, molar volumes and compressibilities (and hence sound velocity) calculated from the theory agree with experimental determinations.

Table I gives the variations of osmotic and activity coefficients with concentration for aqueous solutions of caesium bromide.[40] Figures vary only slightly from earlier values published by Robinson.

When electrolytes are dissolved in water there is normally a decrease in volume which according to the theory of Drude and Nernst is due to the accumulation of water molecules around the ions of the electrolyte in their vicinity in such a way that the density of the water increases. Relatively concentrated solutions of caesium bromide, however, show an increase in

TABLE I.- VARIATION WITH CONCENTRATION OF OSMOTIC AND ACTIVITY COEFFICIENTS FOR AQUEOUS CAESIUM BROMIDE AT 25°C.

m (moles/1000 g. H_2O)	Osmotic coefficient ϕ	Activity coefficient γ
·1	·917	·754
·2	·896	·694
·3	·882	·654
·4	·873	·626
·5	·865	·603
·6	·861	·586
·7	·857	·571
·8	·854	·558
·9	·852	·547
1·0	·858	·538
1·2	·849	·523
1·4	·848	·510
1·6	·848	·500
1·8	·850	·493
2·0	·852	·486
2·5	·859	·474
3·0	·866	·465
3·5	·874	·460
4·0	·884	·457
4·5	·892	·455
5·0	·901	·453

volume and no satisfactory explanation has been given for this effect.[41]

The solubility of cæsium bromide in certain organic solvents is shown in Table II.[42]

TABLE II.- SOLUBILITY OF CAESIUM BROMIDE IN METHYL ALCOHOL, ACETONITRILE AND FORMIC ACID

Temp. °C.	Methylalcohol			Acetonitrile			Formic acid		
	d	*s*	*c*	*d*	*s*	*c*	*d*	*s*	*c*
18	·806	2·1	$8·0 \times 10^{-2}$	·785	·10	3×10^{-3}	1·74	69	3·3
25	·801	2·2	$8·3 \times 10^{-2}$	·782	·14	5×10^{-3}	1·74	71	3·4

[*d* = density; *s* = solubility in g./100 g. solvent; *c* = concentration in mols./litre]

The solubility of ethyl acetate in aqueous solutions of cæsium bromide is given in Table III.[43] **The experimental activity coefficients of ethyl acetate in ·100 M. and ·200 M. cæsium bromide solution are 1·030 and 1·059 respectively.**

TABLE III.- SOLUBILITY OF ETHYL ACETATE IN AQUEOUS SOLUTIONS OF CAESIUM BROMIDE

Concn. CsBr	20°	25°	30°	35°	40°
·100 M.	8·14	7·81	7·48	7·15	6·82 g. ethylacetate/100 g. H_2O
·200 M.	7·93	7·60	7·27	6·94	6·61 g. ethylacetate/100 g. H_2O

The integral heats of solution $L_m^{D_2O}$, $L_m^{H_2O}$ of cæsium bromide in D_2O and H_2O are −7·060 and −6·267 kg.-cal./mol. of salt respectively. The difference in integral heats of solution ($L_m^{D_2O} - L_m^{H_2O} = \Delta L$), called the 'isotopic effect', is − 0·793 kg.-cal./mol. salt. The differences in 'isotopic effect' of two similarly charged ions e.g. Br^- and Cl^-, calculated from the corresponding ΔL values, are independent of the common oppositely charged ion.[44]

On considering the Faraday effect of strong electrolytes in aqueous solution it is found that the corrected molecular rotation of caesium bromide decreases with increasing concentration.[45] The corrected molecular rotation extrapolated to infinite dilution is given approximately by the sum of the corrected ionic rotations.

Measurement of the adsorption of caesium bromide at 25°C., from a 0·01 M. solution saturated with lead sulphide and lead sulphate, by precipitated lead sulphide indicates that the amount adsorbed does not depend on the ability of the adsorbed compound to fit the space lattice of the adsorbent or on the ability of the lead sulphide to orient the crystallization of the salt. The amount adsorbed increases as the molar fraction solubility of the salt in water decreases.[46]

Chemical properties

A double salt, $CsBr,MgSO_4$, of the anhydrous kainite type $KCl,MgSO_4$ has been obtained. The electrical conductivity of the fused kainite system has a sharp minimum at the molar ratio 1:1, indicating a decrease in the number of ions, *i.e.* persistence of the complex ions characteristic of kainite even in the fused state. The electrical dissociation is probably into $[Cs]^+$ and $[BrMgSO_4]^-$. The formation of the kainite is thus contingent on the relative attraction of Cs^+ and Mg^{++} for Br^- and is determined by the generalized moment $\mu = Z/r$ where Z = charge, r = radius of the ion.[47]

Potentiometric studies of the reaction between 0·2 N. calcium ferrocyanide and approximately 0·1 N. CsBr have shown a break in the curve of equivalence points indicating the equilibrium: $Ca_2Fe(CN)_6 + 2CsBr \rightleftharpoons CaBr_2 + CaCs_2Fe(CN)_6$, and thus confirming the composition of the double salt. However, the agreement is not sufficient from a quantitative point of view to make the use of this reaction possible for the potentiometric determination of the caesium in this way.[48]

In the manufacture of selenium rectifier plates about 0·005–0·5% of caesium bromide is added to selenium; a layer of the mixture is applied to a supporting electrode, the selenium is transformed into its grey crystalline form, a blocking layer is formed over the treated selenium surface and a counter electrode is applied over the treated selenium surface. An alternative addition agent is 0·005–0·5% of caesium hexabromoselenate.[49]

The addition of caesium bromide in small amounts to a pure selenium rectifier plate coated with a ternary (Sn–Cd–Bi) eutectic alloy decreases the resistance markedly in the positive direction.[50]

When caesium bromide is ground up with a thallous salt a phosphor is formed which has a visible luminescence, but its intensity is far weaker and the colour somewhat more greenish than that produced by potassium salts.[51]

CAESIUM POLYBROMIDES AND COMPLEX BROMIDES

Time–composition curves indicate the existence of $CsBr_4$, $CsBr_3$ and CsBr but not of $CsBr_2$. Because of the loss of bromine from caesium tetrabromide on drying, an indirect method of analysing the solution must be used. Caesium bromide is dried in a stoppered bottle and weighed amounts of bromine and water are added and the bottle shaken for 3 days. The contents are then decanted into a calibrated flask, some ammonium iodide is added and the solution made up to the mark. Part is then titrated with 0·1 N. H_2SO_4 standardized simultaneously with standard iodine solution. Another part is evaporated to dryness to drive off the ammonium salt and then converted to the chloride.[52]

Examination of the system caesium bromide–bromine–water at 0°C. and

25°C. shows[53] that the only polybromide existing at these temperatures is the tribromide $CsBr_3$, and the study at 0°C. confirms the composition of bromine hydrate as $Br_2,10H_2O$.

Solutions of cæsium bromide in molten iodine bromide show high conductivity and investigation by conductometric titration shows the following reaction: $2CsIBr_2 + SnBr_4 \rightleftharpoons Cs_2SnBr_6 + 2IBr$. There are few good acids in the iodine bromide system owing to the instability of complex bromides.[54]

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SECTION LXXXIX

CAESIUM IODIDE

By N. R. W. BENWELL

Physical Properties

X-Ray diffraction patterns of cæsium iodide taken at temperatures up to the melting point give no evidence of any transition from simple cubic to face-centred cubic structure similar to the transition which occurs in caesium chloride at 469°C. Consideration of the molar volumes of the solid and liquid salts at the melting points leads to the conclusion that the structural alteration from 8 to 6 fold co-ordination, which in cæsium chloride takes place in the solid phase at 469°C., occurs in the case of cæsium iodide at the melting point as part of the fusion process. The percentage volume expansion of cæsium iodide on melting of 28·5 is essentially equal to the sum of the expansions for cæsium chloride at the transition and melting point, 17·1 + 10·0 = 27·1%.[1]

Powder diffraction patterns of cæsium iodide from 22°C. to 36°C. give a linear coefficient of expansion[2] of $4{\cdot}86 \times 10^{-5}$ per °C. and a lattice constant of 4·5667 A. at 20°C. The melting point of cæsium iodide is 621°C. and at 0°C. its solubility in water is 44 g./100 g. H_2O (cf. Table VI). As a transmitter of infra-red light, caesium iodide compares favourably with cæsium bromide and thallium bromide iodide,[3] being transparent from 0·242μ to >50μ. A fair agreement with that obtained from experimental data is found[4] when the thermal expansion of caesium iodide is calculated from Frenkel's expression for ionic crystals:

$$a = [(n + 4)/2(n - 1)][c/W_k]$$

where n = exponent in the expression which characterises the energy of the repulsive forces; c = heat capacity per. g.-atom; W_k = coulomb portion of the energy of the ionic crystals as calculated by Madelung.

The vapour pressure of cæsium iodide (crystal) is given by the equation:[5]

$$\log_{10} P_{\text{dynes}} = -10{,}360/T + 13{\cdot}793$$

in the temperature range 767–847°K. The heat of sublimation is 47,500 g.-cal. per mole and the vapour is unimolecular. Vapour pressure data measured between pressures of 0·0001 and 0·1 mm. by means of a diffusion method using an oxide coated tungsten filament as detector, fit the equation:[6]

$$\log p_{\text{mm.}} = C - A(1000/T) + 5/2 \log(1000/T)$$

Values of A and C for caesium iodide are 11·193 and 11·726, respectively. Heat content (heat of vaporisation) at 800°K. = 47·23 ± 0·28 kg.-cal./mole. Entropy of vaporisation at 800°K. = 59·04 g.-cal./degree.

The heat of vaporisation has also been determined[7] from the expression: $\lambda = -1{\cdot}985 \times 2{\cdot}303 \times [d \log p/d(1/T)] = 44820$ g.-cal. The same author gives the boiling point as 1280°C. by calculation or extrapolation of vapour pressure data, and a critical temperature of 2407°K. For gaseous cæsium iodide, the interatomic distance is 3·36 A., fundamental frequency = 160 cm.$^{-1}$ and entropy ($S_{298\cdot1}$) = 63·1 g.-cal./degree.[8]

The vapour pressure curves of the alkali metal iodides at temperatures between the boiling point and 200—300°C. below the boiling point of the salt lie closer together than those of the fluorides, chlorides or bromides.[9]

When an aqueous solution of caesium iodide is evaporated slowly, the rhombic dodecahedral form (110) is obtained. At high rates of evaporation, the cubic form (100) is obtained. For low rates of evaporation (low degrees of supersaturation), planes with low electric fields, *i.e.* planes containing both cations and anions, form the faces (110) for the CsCl-type lattice of caesium iodide. For high rates of evaporation, planes consisting of either cations or anions form faces (100) for the CsCl-type lattice.[10] In considering transition from homopolar to ionic bond, it is the importance of the van der Waals forces which decides the nature of the lattice structure in the case of the alkali halides: caesium iodide is strongly polarisable and has the CsCl-type lattice.[11] Conversely in considering the effect of the eigenfunctions of the outer electrons in ions (directional forces) on the type of lattice formed it is stated that for univalent ions of large size such as those of caesium iodide, the polarization forces are negligible.[12] The dipole moment of caesium iodide determined experimentally[13] is $12\cdot1 \times 10^{-18}$ at 873°K.; this indicates a mixture of the ionic and homopolar types of bonding and favours the conclusion that the salt vapour contains single molecules only.

Calculations, by means of a Debye formula, of the permanent electric moment of caesium iodide in which the ions have a rare gas structure gives a result at variance with the experimental value.[14] The difference is ascribed to deformation of the external electron shell. The magnetic susceptibility of caesium iodide has been measured[15] by placing the crystals in a glass tube suspended from a balance and bringing the sample midway between the poles of an electromagnet. Values obtained were $78\cdot8 \times 10^{-6}$ and $76\cdot4 \times 10^{-6}$. On the assumptions that the constituent elements are in the ionic condition and that the susceptibility is proportional to the square of the atomic numbers, for caesium, susceptibility = $-38\cdot0 \times 10^{-6}$ and $-36\cdot8 \times 10^{-6}$; for iodine $-40\cdot8 \times 10^{-6}$ and $-39\cdot6 \times 10^{-6}$.

Calculations of the dielectric constant of caesium iodide by various methods differing in the evaluation of the ionic polarizability give values in satisfactory agreement with experimental data. The evaluation is based[16] on the calculation of an elastic force coefficient k between opposed ions as the second derivative of the repulsion energy, from formulae of the type:

$$k = 1\cdot16(n-1)q^2/r_0^3$$

where n = exponent of repulsive energy law; q = charge of the ion; r_0 = nearest distance in the lattice.

Determination of the thermal dissociation equilibrium of caesium iodide by measurement of the current carried by the alkali or iodide ions has been used to calculate the electron affinity of iodine.[17] From the equilibrium, the free energy of dissociation into ions is calculated and by using known values of the heat of dissociation into atoms and the ionizing potential of the alkali atoms it is possible to calculate the electron affinity of the reaction:

$$\mathrm{I^-_{gas}} \rightarrow \mathrm{I_{gas}} + \mathrm{E^-_{gas}} \text{ at } 0^\circ\text{C. abs.,}$$

$\mathrm{E^-_{gas}}$ being an electron. The value found, 72·6 ± 2kg.-cal., agrees well with that calculated from Born's lattice theory.

When caesium iodide (having the CsCl-type structure) is deposited by evaporation on cleavage surfaces of mica, lithium fluoride, sodium chloride, potassium bromide, potassium iodide and calcium carbonate, electron diffraction examination has shown that the crystals touching the substrate have the NaCl-type structure. The lattice parameter a_0 for the NaCl-type crystal is 7·66 A. and the interatomic distances are lower than in the CsCl-type structure.[18]

The calculation of the forces between molecules of argon and the body-centred caesium iodide crystal shows that the single ion in the second layer exerts more force than the four ions in a square in the surface of the cleavage layer. This force is greater than that due to the simple cubic potassium chloride. The variation of heat of adsorption with fraction of surface covered is less than might be expected because of the opposed effects of the electrostatic forces and van der Waals forces.[19]

A sufficiently sensitive experimental technique has been used to measure accurately the very small amounts of non-polar gas adsorbed on cæsium iodide crystals (from 0·20 to 0·30 cu.mm. per g. of salt) in the temperature range from 65°K. to 90°K. Isotherms for argon, oxygen and nitrogen have been determined and heats of adsorption for argon, oxygen and nitrogen are 4·5, 4·0 and $4{\cdot}0 \times 10^6$ g.-moles. The position at which the first monolayer is completed is found to be given by a maximum when ΔH is plotted as a function of the amount adsorbed. Experimental and theoretical values are in good agreement and where divergence of the curves occurs, this can be ascribed to adsorption taking place in cracks and other irregularities. In the region between the completion of the monolayer and the bulk condensation of a gas, an amount equal to three to four times the first layer is adsorbed; the molecules are arranged in layers rather than in localized aggregates.[20] Other authors have measured the adsorption of carbon monoxide, nitrogen, argon and oxygen by caesium iodide between 65·5°K. and 91·6°K. Heats of adsorption are calculated from the Clausius–Clapeyron equation and, within ±100 g.-cal. in the range 0·2 to 0·8 coverage, they show no definite trend with temperature. Over the initial region of decreasing heat with coverage, the $\log p$ against $\log X$ plots are accurately linear for argon, oxygen and nitrogen. The initial decrease in the heat of adsorption of argon, oxygen and nitrogen with coverage is attributed to the non-uniformity of the cæsium iodide crystal surface. The results have been used to test the effects of surface heterogeneity, lateral interaction and secondary-layer formation on the heat of adsorption and on the form of the adsorption isotherm. The equilibrium form of cæsium iodide is a rhombic dodecahedron and in consequence adsorption takes place on the (110) and not on the (100) surface. The same authors have determined the adsorption of two binary gas mixtures, nitrogen and carbon monoxide at 83·6°K. and argon and oxygen at 77·5°K., by cæsium iodide. The total amounts of the two gases for each composition originally admitted were in a fixed ratio. Nitrogen and carbon monoxide mixtures follow a "mixed" Langmuir equation and any deviations are primarily due to the failure of the single-gas Langmuir equation to account for the adsorption of the individual gases. The adsorption of oxygen and argon follows the Freundlich equation. This is due to (1) the much lower net heats of adsorption of oxygen and argon which allow multilayer adsorption to occur well before the monolayer is complete, and (2) in the lower pressure range the amounts of these two gases adsorbed are smaller and deviations from the Langmuir equation due to heterogeneity are more marked.[21]

The root mean square amplitude of atomic vibration at 293°K. is given as 0·33 for cæsium iodide (Lonsdale).[22] The frequencies and anharmonicities of the lattice oscillations of cæsium iodide, *i.e.* the oscillations of the interpenetrating lattice of the cæsium and iodine ions with respect to one another have been calculated on the basis of the Born model. The calculated value of the frequency of lattice oscillation, $1{\cdot}8 \times 10^{-12}$, is in good agreement with observed values (Krishnan and Roy). The anharmonicity of the lattice oscillation, unlike its frequency, varies with the direction of the oscillation from a large positive value along [111] to a small negative value along [100].[23]

The intensity of orbital interaction of salts with ions of elements of atomic number one above or below the rare gases (*i.e.* with 6p electrons) is calculated[24] from the equation:

$$T = F\sqrt{N}$$

where T = m.p. in °K.; N = no. of orbital contacts. For cæsium iodide, where $N = 12$, $F = 258$.

Molar refraction and ion distance determinations for alkali halides of noble gas shell such as cæsium iodide, lead to ion radii and polarizability values in good agreement with values determined by other methods, indicating that univalent ions of the same shell structure do not deform themselves in such lattices. The ratio of the radii in such lattices is always approximately = 0·73. From the ion radius, ion refraction and polarizability are also in good agreement with similar values calculated theoretically or empirically. For α-cæsium iodide, ion distance = 3·828 A., molar refraction = 26·3 cm.^{3}, (25·1); ion radii = 1·62 A. for Cs^+, 2·2 A. for I^-, (1·65, 2·2; 1·69, 2·16); ion polarizability = 2·37 A.^{3} for Cs^+, 6·58 A.^{3} for I^-, (2·56, 7·55). Brackets give theoretically and empirically calculated values.[25]

When silver halides are combined with the corresponding alkali halide, the phase diagrams show certain regularities: with the chlorides, lithium and sodium form solid solutions, potassium and rubidium form eutectics and cæsium forms a peritectic; with the bromides, lithium and sodium form solid solutions, potassium forms a eutectic, and rubidium and cæsium peritectics; and with the iodides, only lithium forms a solid solution, sodium a eutectic and potassium, rubidium and cæsium peritectics. The change from one type of diagram to the other is explained by the formation of complexes.[26]

The system cæsium–cæsium iodide shows complete miscibility at and above the melting point of the salt. The temperature–concentration range of coexistence of two liquid phases which, in analogous systems, decreases from sodium to potassium, disappears altogether for the Cs–CsI system. The solubility of the solid halides in the corresponding liquid alkali metals at a given temperature increases greatly with the atomic number of the metal, owing to a decrease of cohesive forces in both the metal and its salts as the atomic number increases. In the case of cæsium with its relatively low cohesive energy (heat of vaporisation = 16·3 kg.-cal.), the "substitution" of anions for electrons in the metal also requires a relatively low energy. The cohesive energy or heat of sublimation of cæsium iodide = 38 kg.-cal. and the heat of solution = 18 ± 1 kg.-cal.[27]

The cubic compressibility of cæsium iodide is 9·3 per megabar × 10^{-6} as derived from the semi-empirical equation

$$\beta = kV_m/U$$

where β = compressibility; k = empirical constant; V_m = molecular volume; U = molecular heat of formation of the salt.[28]

The compressions of cæsium iodide under 50,000 kg. per sq.cm. at room temperature and at the temperature of solid carbon dioxide are 0·2025 and 0·1928 respectively.[29] The compression for the decrement 50,000–100,000 kg./sq.cm. is 0·086 at room temperature.[30]

By directing a molecular beam of cæsium iodide at a thoriated tungsten wire (at 1200–1500°K.) yields of iodine negative ions have been obtained. The maximum and stable yields were 4% and 2% respectively and are considerably less than yields of negative ions obtained with cæsium chloride or bromide. No molecular ions were produced. The yield from pure tungsten surfaces was much lower.[31] Caesium iodide is effective as an activating agent in the selenium rectifier. Small traces of cæsium iodide in the selenium plate coated with a ternary (tin–cadmium–bismuth) eutectic alloy decrease the resistance considerably in the positive direction but increase it in the negative direction. In this respect cæsium iodide is a more effective activating agent than cæsium bromide or cæsium chloride which has practically no activating effect.[32]

Caesium iodide is one of a number of iodides which have been examined as a catalyst in the production of tetraethyl and tetramethyl lead made by the reaction of finely divided lead with ethyl or methyl chloride or bromide but its catalytic value is not high with respect to this reaction.[33]

The stability of caesium iodide sulfone, $CsI,3SO_2$, is indicated by the dissociation tension in mm. at various temperatures as follows: at −22·5–8°C., 51; at 0°C., 269·25; at 15·4°C., 704; at 16·46°C., 760.[34]

Ramsey has shown that chemical shifts result from precessional motions induced by the applied magnetic field in the electrons surrounding the nucleus. This precessional motion produces a small local field at the nucleus in opposition to the applied field and this local field will vary from molecule to molecule as a result of the variations in electronic structure. 100% ionic compounds have no chemical shifts and so the shielding change observed for caesium iodide indicates that there is some covalent character in the crystalline bond. The chemical shift of the ^{133}Cs magnetic resonance,

$$\Delta\sigma = (H_s - H_r)/H_r \times 10^4,$$

where H_s and H_r are the magnetic fields necessary for resonance at a fixed frequency for the sample and reference respectively, is −2·52 for cæsium iodide, the reference being a saturated aqueous solution of cæsium chloride. The magnetic shielding of the alkali metals decreases from the fluoride to the iodide, while the ion in solution has the largest shielding of all.[35]

The supersaturation limit for caesium iodide in aqueous solution is calculated from the formula: $T_s - T = 13\sigma V_m/\lambda$ where T_s = absolute saturation temperature; T = absolute temperature of the first spontaneous crystallisation; σ = specific surface energy; V_m = mol. volume; λ = heat of solution. Experimental values given are: $\lambda = 8104$; $\sigma = 106$; $\sigma V_m = 6112$, giving $T_s - T = 9{\cdot}6$°C. The radius of the stable crystal nucleus at the first temperature of spontaneous crystallisation is shown to be of the order of 10^{-6} cm. and varies hyperbolically with the degree of supersaturation.[36]

The total heat of hydration $H^{\pm}$ (kg.-cal./mole) of cæsium iodide has been selected on the basis of measurements of heats of solution at infinite or very high dilution and values of lattice energy U although the latter term involves an uncertainty of thermodynamic definition.[37] The value given for cæsium iodide is 127 kg.-cal./mole. As a principle for separation of $H^{\pm}$ into heats of solvation H^+ and H^- of the individual ions, Mishchenko rejects assumptions made by Bernal, Fowler and other workers and ascribes equal heats of solvation to Cs^+ and I^- ions on the assumption that the difference in their radii is compensated by the H_2O dipole moment dissymmetry. On this basis, heats of solvation of Cs^+ and I^- become 63 and 63 kg.-cal./g.-ion respectively. Co-ordination numbers, n, (no. of mols. of water surrounding the ion in the nearest solvate envelope) are for Cs^+, 8 and for I^-, 8 and are evaluated from the known radii of the ions and the radius r_w of the water molecule. Reasonable values are obtained with $r_w = 1{\cdot}93$ A. corresponding to liquid H_2O but not with $r_w = 1{\cdot}38$ A., the radius of H_2O in ice. The values are at considerable variance with those of Bernal, Fowler and others who attribute $n = 4$ to all univalent ions on the assumption of a "frozen" hydrate envelope. The ratio of the heat of solvation H_1 and the co-ordination number n gives the heats of interaction H_1 between the ion and 1 mol. water in the solvate envelope as 7·9 kg.-cal./g.-ion for Cs^+ and 7·9 kg.-cal./g.-ion for I^-. These values can be represented as a function of the ionic radii in the form: $\log H_1^- = (1{\cdot}38/r^-) + 0{\cdot}25$; $\log H_1^+ = (0{\cdot}70/r^+) + 0{\cdot}47$ and $(1/H_1^-) = 0{\cdot}1\,r^- - 0{\cdot}085$; $(1/H_1^+) = 0{\cdot}1\,r^+ - 0{\cdot}035$. Simple consideration of electrostatic interaction gives per mol. H_2O an energy of $127{\cdot}06 \times 10^{-16}/(r_i + r_w \pm \beta)^2$ kg.-cal./g.-ion. Values calculated with this formula are in very fair agreement with the experimental heats of solvation for Cs^+ and I^- with $\beta = 0{\cdot}25$ and $r_w = 1{\cdot}93$ A. The effective radii of water molecules in the hydrate envelope of Cs^+ and I^- have been calculated to be 1·10 A. and 2·09 A. respectively, which being greater than 1·93 A. indicate an expansion of the hydrate envelope.

From standard electrode potentials of iodine and caesium and from relevant free energy data, Kanevskiĭ has calculated the standard free energy of hydration of the ions Cs^+ and I^- to be 126·0 kg.-cal. per mole.[38]

The specific heat capacity of cæsium iodide in aqueous solution of 10·40% concentration is 0·8834 g.-cal./g.degree. The extrapolated molar heat capacity (C) of caesium iodide at infinite dilution is −31·8 ± 1 kg.-cal./mol.-degree calculated from the equation $C = (277/r_{aq.}) - 31{\cdot}1\,e$, assuming that C for caesium = C for iodine, e = formal charge on the ion. The inverse "aqueous" ionic radius ($1/r_{aq.}$) is calculated on the assumption that caesium ions and iodine ions have the same radius in solution.[39]

The fluidity ϕ of aqueous solutions of cæsium iodide is given by the equation of Jones and Dole:[40]

$$\phi = 1 - A\sqrt{c} - Bc \quad (c = \text{concentration in M./litre.}).$$

The equation holds up to $c = 0{\cdot}1$ at 0°C. and 0·2 at 25°C. By addition of a term Dc^2 the equation holds to 1·44 M. A is calculated from the Debye theory but experimental results are not in very good agreement with the theory of Falkenhagen and Vernon on the effect of interionic attractions on the viscosity. The density of the solutions is calculated from Root's equation

$$D_4^{25} = 0{\cdot}99707 + 0{\cdot}20225c - 0{\cdot}00162c^{3/2}$$

valid for concentrations to 2 N. Caesium iodide is found to be more effective in lowering the viscosity of water than any other known salt. Equivalent ionic conductances at 0°C. are for Cs^+, 44·4; I^- 43·4 and at 25°C. for Cs^+ 78·1; for I^- 76·7.

In introducing the concept of closest approach of ions in an extension of the theory of the conductivity and viscosity, it is assumed that the ions are of finite size, having a distance of closest approach (a). Various derivations of a for caesium iodide are as follows: from the osmotic coefficient, 3·75 A.; from conductivity, 3·0 A. (at 0°C.); from ionic mobility, 2·38 A.; from crystallographic data of ionic radii (Pauling), 3·85 A. The theory is valid for concentrations up to 0·1 N. in the case of conductivity but appears to be invalid in the case of viscosity.[41]

When electrolytes are dissolved in water there is normally a decrease in volume which, according to the theory of Drude and Nernst, is due to the accumulation of water molecules by the ions of the electrolyte in their proximity in such a way that the density of the water increases. Solutions of cæsium iodide however show an increase in volume and no satisfactory explanation has been given for this effect.[42]

Surface tension measurements of aqueous solutions of cæsium iodide show that the surface tension–concentration curve passes through a minimum if no wetting film correction is made; *i.e.* at sufficiently low concentrations the salt decreases the surface tension of the solution and is "capillary active" and according to Gibbs' theorem the salt is positively adsorbed, while at moderate and high concentrations the salt is "capillary inactive" and increases the surface tension of the solution.[43] In Table I the figures in column 4 should be constant if surface tension $\propto$ concentration.

TABLE I.- VARIATION FOR CAESIUM IODIDE OF SURFACE TENSION AND DENSITY WITH CONCENTRATION AT 25°C.

c(g.moles/l.)	D_c	σ_c/σ_0	$(\sigma_c-\sigma_0)/c\sigma_0$
·0001	·997101	·99995	−0·5
·0002	·997119	·99986	−0·7
·0005	·997183	·99984	−0·32
·0010	·997288	·99987	−0·13
·0020	·997474	·99991	−0·045
·0050	·998101	·99998	−0·004
·0100	·999100	1·00010	+0·010
·0200	1·001118	1·00038	+0·019
·0500	1·017179	1·001010	+0·0202
·1000	1·017258	1·001930	+0·0193
·2000	1·037389	1·003610	+0·0181

The density is expressed by means of Root's equation:

$$D^{25}_{4} = 0{\cdot}997074 + 0{\cdot}182105c - 0{\cdot}015075c^{3/2}$$

Determination of the refractive index, n, of aqueous caesium iodide solutions in the concentration range 0·002–0·0002 N. shows that the difference in refractive index between solution and solvent is a linear function of the square root of the concentration from 0·002 N. down to a concentration which depends on the type of salt used. The results in Table II indicate absence of ionic deformation.[44]

TABLE II.- VARIATION OF REFRACTIVE INDEX WITH CONCENTRATION FOR AQUEOUS SOLUTIONS OF CAESIUM IODIDE

Concn. (Normality)	Refractive Index $n(\delta n \times 10^6)$
·002	52
·0016	44·4
·0013	37·1
·0010	28·1
·0009	25·3
·0008	22·5
·0007	19·6
·0006	17·0
·0005	13·9
·0004	10·8
·0003	8·2
·0002	5·6

Table III gives the variations of osmotic and activity coefficients with concentration for aqueous solutions of caesium iodide: these figures differ only slightly from earlier values published by Robinson.[45]

Table IV gives the solubility of caesium iodide in certain organic liquids.[46]

Attempts have been made to correlate the solubility of caesium iodide and other alkali halides in various alcohols, acetone and water with the dielectric constant of the solvent but because of the many factors involved no general rule has been established. In contrast to that in the other solvents,

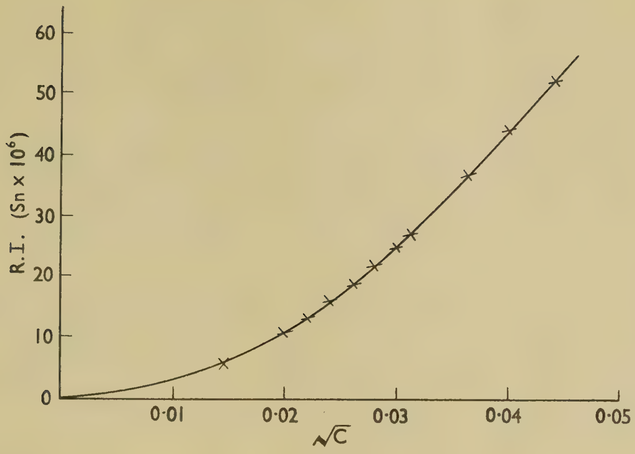

FIG. 1.- REFRACTIVE INDEX—CONCENTRATION CURVE FOR AQUEOUS SOLUTIONS OF CAESIUM IODIDE

TABLE III.- VARIATION OF OSMOTIC AND ACTIVITY COEFFICIENTS WITH CONCENTRATION OF CAESIUM IODIDE SOLUTIONS

m (moles/1000 g. H_2O)	Osmotic coefficient ϕ	Activity coefficient γ
·1	·918	·754
·2	·895	·692
·3	·880	·651
·4	·870	·621
·5	·863	·599
·6	·858	·581
·7	·855	·567
·8	·852	·554
·9	·849	·543
1·0	·846	·533
1·2	·842	·516
1·4	·839	·501
1·6	·836	·489
1·8	·834	·478
2·0	·832	·470
2·5	·827	·450
3·0	·822	·434

TABLE IV.- SOLUBILITY OF CAESIUM IODIDE IN METHYL ALCOHOL, ACETONITRILE AND FORMIC ACID

Temp.	Methyl alcohol			Acetonitrile			Formic acid		
	d	*s*	*c*	*d*	*s*	*c*	*d*	*s*	*c*
18°C.	·815	3·0	$9{\cdot}3 \times 10^{-2}$	·789	0·7	$2{\cdot}3 \times 10^{-2}$	1·456	28·1	1·22
25°C.	·813	3·7	0·114	·787	0·9	3×10^{-2}	1·46	29·0	1·29

d = density; *s* = solubility in g./100 g. solvent; *c* = concentration in mols./litre

the solubility of the alkali halides in acetone depends upon the anion.[47] The solubility of cæsium iodide in acetone (in weight -%) from −80°C. to 40°C. is given by the expression:[48]

$$0{\cdot}295 - 3{\cdot}03 \times 10^{-3}\,t - 2{\cdot}79 \times 10^{-5}\,t^2$$

Caesium iodide is a strong electrolyte in acetonitrile and exchanges iodine with C_4H_9I with an activation energy of 18 kg.-cal./mole. The process involves the inorganic I^- ion.[49]

The e.m.f. of the cell $Cs|0{\cdot}01\,N.\ CsI\ in\ CH_3CN|0{\cdot}01\,N.\ AgNO_3\ in\ CH_3CN|Ag$ at 25°C. is 2·2723 volts. The temperature coefficient between 20°C. and 30°C. is -3×10^{-4} volts per degree. The effect of dilution on the e.m.f. is relatively small, showing that the activity coefficient of caesium iodide in acetonitrile is considerably smaller than 1. Caesium iodide gives less than a 2% solution in acetonitrile.[50]

From polarographic studies of caesium iodide at a concentration of less than 1·0 millimole/litre in anhydrous acetonitrile in a supporting electrolyte of 0·1 M. tetrabutylammonium iodide, values of i_d (microamps.), $E_{-1/2}$ and E_0 are as follows: $i_d = 3{\cdot}78$; $E_{-1/2} = -1{\cdot}34$; $E_0 = -2{\cdot}272$. In this system, caesium iodide gives a wave involving one electron reduction with a slope 0·06, indicating a reversible process.[51]

The solubility of ethyl acetate in aqueous solutions of caesium iodide is given in Table V. The experimental activity coefficients of ethyl acetate in 0·100 M. and 0·200 M. caesium iodide solution are 1·003 and 0·999 respectively.

TABLE V.- SOLUBILITY OF ETHYL ACETATE IN AQUEOUS SOLUTIONS OF CAESIUM IODIDE

Concn. CsI	25°C.	30°C.	35°C.	
0·100 M.	8·07	7·68	7·29	g. ethyl acetate/100 g. H_2O
0·200 M.	8·08	7·71	7·34	g. ethyl acetate/100 g. H_2O

For the alkali iodides, the experimental activity coefficients differ considerably from the theoretical activity coefficients calculated from equations based on the assumption of coulombic interactions.[52]

Caesium iodide in 6·9 N. hydriodic acid is not extractable with diethyl ether.[53]

Isotherms for the system mercuric iodide–caesium iodide–water at 0°, 12°, 34°, 54° and 72°C. show the existence of five iodomercuriates:[54] $3CsI,HgI_2$, $2CsI,HgI_2$, $2CsI,3HgI_2$, CsI,HgI_2 and $CsI,2HgI_2$. The first three appear to exist over a considerable range of concentration[55] but CsI,HgI_2 is found only at 0°C. and 12°C. and $CsI,2HgI_2$ at 78°C.

Table VI gives freezing point, solubility and boiling point data for the system caesium iodide–water. The phase diagram based on these data shows a eutectic at −4·0°C. and that the boiling point of the saturated solution corrected to 760 mm. is 109·1°C. (108·6°C. at 740–750 mm.).[56]

TABLE VI.- CAESIUM IODIDE–WATER: TEMPERATURE–COMPOSITION DATA

Soln. + ice		Soln. + vapour		Soln. + CsI		Soln. + CsI	
Temp.	%CsI	Temp.	%CsI	Temp.	%CsI	Temp.	%CsI
−1·2	8·76	100·2	7·63	0	30·6	32·4	50·05
−2·7	18·75	100·6	14·28	1·4	31·41	35·6	51·84
−4·0 *E*	27·45	101·4	29·82	9·3	36·90	45·9	55·54
—	—	103·0	46·31	14·0	39·8	59·3	60·43
—	—	104·8	56·97	15·0	40·3	61·0	60
—	—	107·7	67·84	18·0	41·13	61·3	60·75
—	—	109·1 *S*	71·38	19·4	43·32	77·7	65·24
—	—	109·1 *S*	75 *t*	22·8	47·94	88	67·16
—	—	—	—	25	46·1	102·8	70·25
—	—	—	—	32	49·98	109·1 *B*	71·48

E = Eutectic; *S* = saturated with solid phase; *B* = boiling point; *t* = total composition solid and liquid

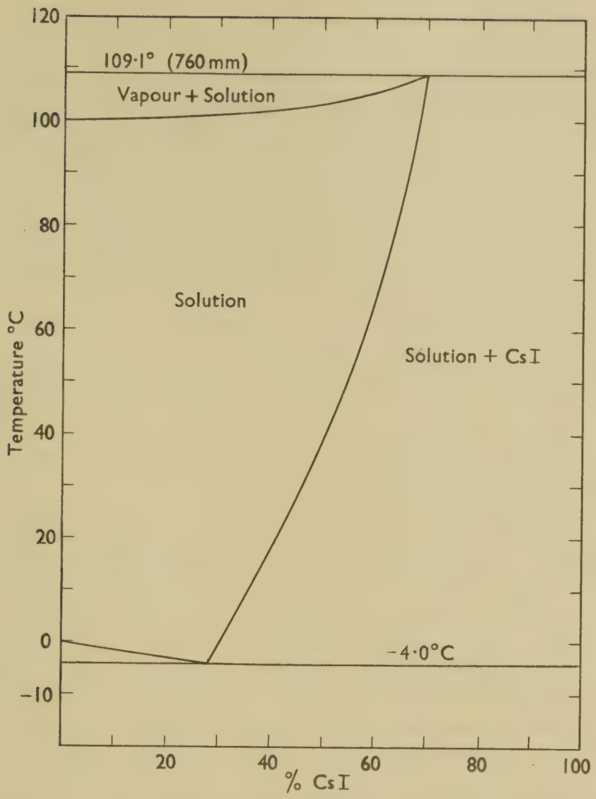

FIG. 2.- THE SYSTEM CAESIUM IODIDE–WATER AT 760 mm.

Chemical Properties

Caesium iodide reacts with sulphamic acid, $HSO_3.NH_2$, to give the tri-iodide, CsI_3. Because of the stability of cæsium tri-iodide both as a solid and in solution, it can be used as a standard for iodometric analysis since iodine is easily liberated. Titrations with tri-iodide solution compare very favourably with titrations employing standard iodine solution.[57]

A double salt $CsI,MgSO_4$ of the type $KCl,MgSO_4$ has been obtained. The electric conductivity of the fused kainite system has a sharp minimum at the molar ratio 1:1 indicating a decrease in the number of ions, *i.e.* persistence of the complex ions characteristic of kainite even in the fused state. The electrical dissociation is probably into $[Cs]^+$ and $[IMgSO_4]^-$. The formation of the kainite is thus contingent on the relative attractions of Cs^+ and Mg^{++} for I^- and is determined by the generalized moment $\mu = Z/r$ where Z = charge, r = radius of the ion.

CAESIUM POLYIODIDES

According to Clark, the crystal structures of cæsium tri-iodide (orthorhombic), caesium dibromoiodide (orthorhombic) and cæsium dichloroiodide (rhombohedral hexagonal) indicate the same relative arrangement of the atoms. The three halogen atoms constituting the complex anionic group lie in a line with the heaviest at the centre on the body diagonals of the unit parallelepiped containing one molecule and thus constitute a singly acting unit in the solid lattice. This is also true of the complex ions in solution. The relative stabilities of the polyhalides are directly related to the lattice dimensions; therefore, other things being equal, sodium atoms are not able to hold three halogen atoms in this kind of spatial distribution and the equilibrium $I^- + I_2 \rightleftharpoons I.I_2^-$ is preponderantly to the left. If the unit parallelepiped of caesium tri-iodide has a diagonal along which lie one Cs and three I diameters, the atomic radii of Cs and I are appreciably smaller than those found in simple halides etc. This is taken to mean that a great compressing force parallel to the diagonal squeezes the atoms together in this direction, agreeing with the known properties, the conception of compressible atoms and with the non-additivity of atomic radii.[58]

Pauling and Bozorth reached different conclusions from a consideration of spectral and Laue photographs and the theory of space groups and assigned the following dimensions to the orthorhombic unit cells, each containing 4 molecules CsI_3: d_{100} = 6·83, 6·80 A.; d_{010} = 9·89, 10·00; d_{001} = 11·00, 11·02. $CsIBr_2$ d_{100} = 6·57; d_{010} = 9·18; d_{001} = 10·66.

The lattice and space group for both are probably Γ_0 and V_h^{16} respectively. The atoms in the units are not placed.[59]

Recent reinvestigation of the crystal structure of cæsium tri-iodide gives the following data:[60] *a* 6·86; *b* 9·98; *c* 11·09 A., space group *Pmcn*, *Z* = 4 mols. per unit cell; the complete structure shows that the I_3^- ion has an asymmetric, non-linear form; Cs–I = 3·92 A. *X*-Ray analysis of cæsium tetraiodide shows a space group $P2_1/a$ with four cæsium tetraiodide molecules per unit cell. The structure consists of Cs^+ ions and flat $[I_3^-.I_2.I_3^-]$ ions, the latter showing a weak interaction between their constituents.[61]

The existence of cæsium pentaiodide has been disproved and the correctness of the formula cæsium tetraiodide confirmed for the higher polyiodide of cæsium. Cæsium iodide was melted with excess of iodide and the mixture exposed to sodium hydroxide in a desiccator. The mixture was weighed at 2–3 day intervals. The loss of weight–time curve showed a definite break corresponding to cæsium tetraiodide. The change of slope also showed that the vapour pressure of cæsium tetraiodide is much less than that of free iodine.[62]

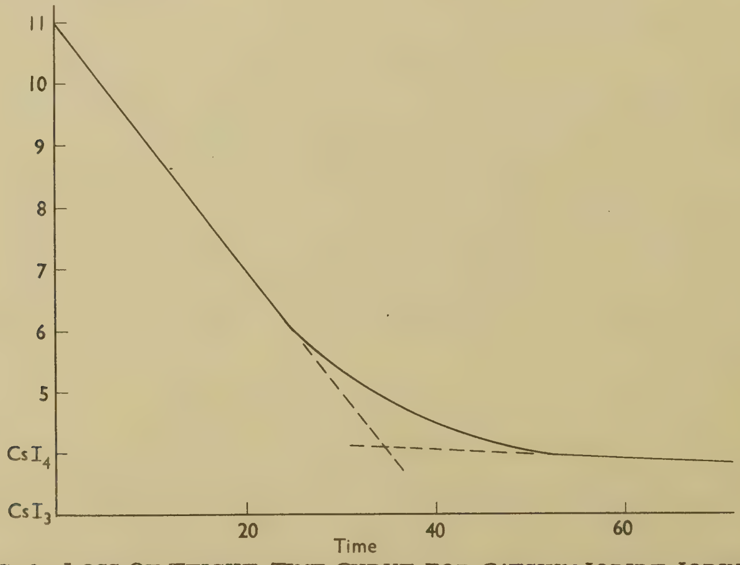

FIG. 3.- LOSS OF WEIGHT–TIME CURVE FOR CAESIUM IODIDE–IODINE

From the diagram of the system caesium iodide–iodine, Fig. 4, the eutectic for 18 mol.-% caesium iodide is fixed at 71·5 ± 0·1. The presence of four solid phases, I_2, CsI_4, CsI_3 and CsI is confirmed but none of these polyiodides is stable at the melting point. A pronounced change of phase is detected at 208–211°C., below which temperature the compound CsI,I_2 (CsI_3) appears. A second point occurs at approximately 136°C. where presumably the compound $2CsI.3I_2$ (CsI_4) begins to form. The diagram further disproves previous reports of the existence of CsI_5.[63] Later work by the same author has established a more accurate value of 140 ± 0·5°C. for the temperature of the transition between the tri-iodide and tetraiodide.

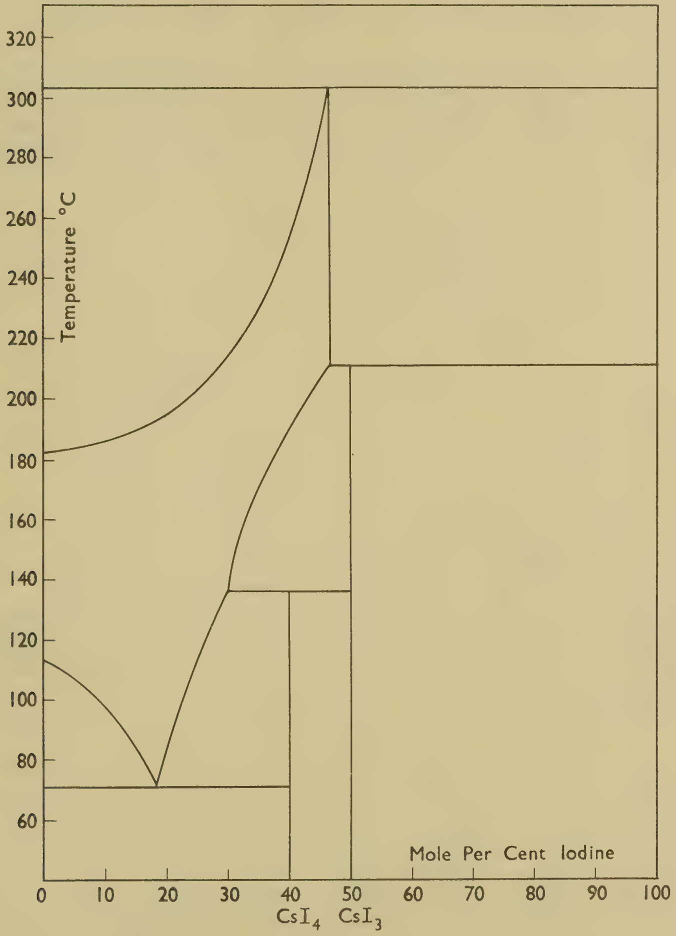

FIG. 4.- THE SYSTEM CAESIUM IODIDE–IODINE AT 745 mm.

In dilute solutions of caesium iodide and iodine in ethyl alcohol pronounced anomalies in density and viscosity have been observed of such a character that they indicated the apparent existence of I_3^-, I_5^- and I_7^- ions with smaller proportions of CsI_3, CsI_5 and CsI_7. No anomalies were found with CsI_4 and CsI_9. Under some conditions, dilute alcoholic solutions of caesium iodide showed a "negative viscosity."[64]

Caesium tetraiodide is diamagnetic and is therefore correctly formulated as Cs_2I_8 and not CsI_4 which would have a strong component of paramagnetism owing to the unpaired electron of the I_4^- ion. The magnetic susceptibility is close to the calculated value. The stability of Cs_2I_8 and CsI_3 is ascribed to resonating configurations in the polyiodide groups.[65]

Solubility determinations in benzene and toluene at 6°C. and 25°C. prove the existence of the binary compounds caesium tri-iodide and caesium tetra-iodide. In benzene, a ternary compound, $CsI{-}9I{-}2C_6H_6$ is also found. From solubility data, the following dissociation pressures are calculated: for CsI_3 at 6°C. –0·000131 mm.; at 25°C., 0·000970 mm.; for CsI_4 at 6°C. –0·00775 mm.; at 25°C., 0·04790 mm. giving heats of dissociation, by van't Hoff's equation, for CsI_3, –17,500 g.-cal., and for CsI_4, –15,800 g.-cal.[66] The dissociation pressures of caesium tri-iodide are lower than those of rubidium tri-iodide.[67]

Fig. 5 shows the phase diagram for the ternary system caesium iodide–iodine–water in air at 740–750 mm.[68] The solid phases are ice, iodine, caesium iodide, caesium tri-iodide and caesium tetraiodide. The ice field is almost invisible in Fig. 5a, but may be seen in part in the enlarged section (Fig. 5b).

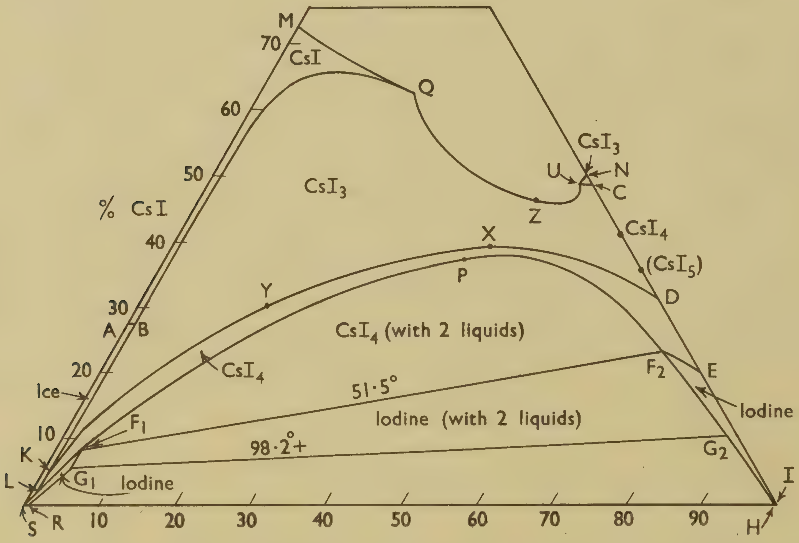

FIG. 5a.- THE SYSTEM CAESIUM IODIDE–IODINE–WATER AT 740–750 mm.

The field of the tri-iodide extends over a very wide area of the projection diagram, while a large part of the tetraiodide and iodine fields is masked by the binodal region. There are 4 ternary invariant points below the vapour region: *viz:* *B* at –4·0°C. for ice–caesium iodide–caesium tri-iodide–liquid; *K* at –0·5°C. for ice–caesium tri-iodide–caesium tetraiodide–liquid; *L* at –0·2°C. for ice–caesium tetraiodide–iodine–liquid and F_1F_2 at 51·5°C. for caesium tetraiodide–iodine–two conjugate liquids. Point *B* is the only ternary eutectic and there are no dystectic points on any of the field boundaries.

Starting at the lowest point *B*, there is a rise along *KB* (ice–caesium tri-iodide–liquid) in the direction of *L*, along *SL* (ice–iodine–liquid) in the direction of *S*, along *BQ* (caesium iodide–caesium tri-iodide–liquid) in the direction of *Q*, along *AB* (ice–caesium iodide–liquid) in the direction of *A*

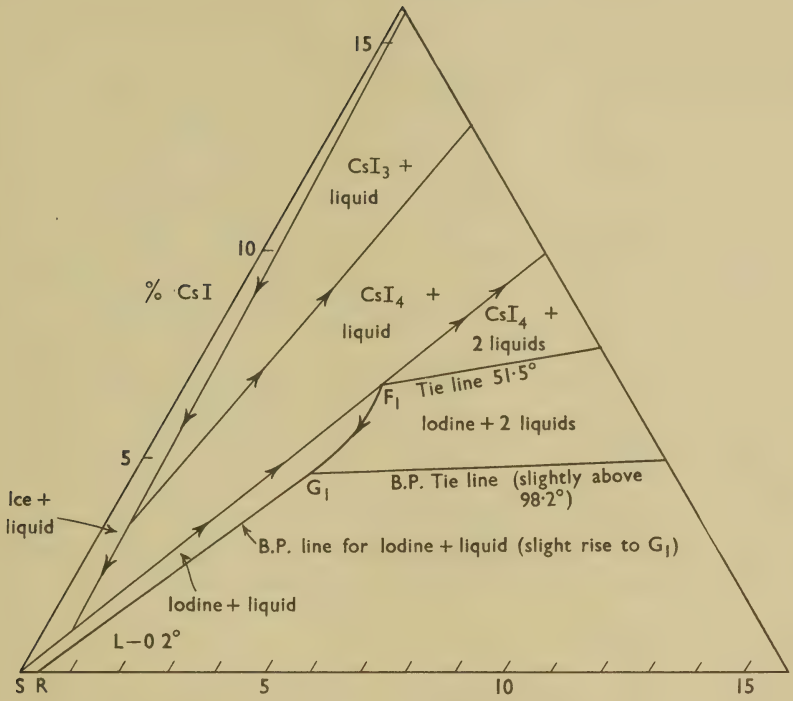

FIG. 5b.- PART OF FIG. 5a ENLARGED

(although the temperature difference is hardly enough to be experimentally detectable). There is also a very abrupt rise along *UC* (caesium iodide–caesium tri-iodide–liquid) in the direction of *C*, along *KD* (caesium tri-iodide–caesium tetraiodide–liquid) in the direction of *D*, along LF_1 (caesium tetraiodide–iodine–liquid) in the direction of F_1 and along F_2E (caesium tetraiodide–iodine–liquid) in the direction of *E*. All these temperature rises accord with the theorem of van Alkemade as interpreted by Bancroft. As to the binodal boundaries, the temperature rises along G_1F_1 and passes through a maximum on F_1PF_2 (caesium tetraiodide–2 conjugate liquids) at *P* (plait point saturated with caesium tetraiodide). It should be noted that the temperature rise along *KD* is abrupt at first, then gradual then abrupt again as the line nears *D*. The rise is also abrupt along LF_1 and moderately so along F_2E. The condensed boundary *UC*, the exact position of which is uncertain, is a continuation of *BQ* (caesium iodide–caesium tri-iodide–liquid) and F_2E is a continuation of LF_1 (caesium tetraiodide–iodine–liquid). Under the pressure prevailing (740–750 mm.) the complete boundary curve from *B* to *C* is broken into separate parts *BQ* and *UC* because it intersects the ternary boiling point surface at *Q* (109·6°C.) and *U*. The break in the other boundary curve is due to the fact that the simple liquid phase splits into 2 conjugate solutions at F_1F_2 (51·5°C.).

Table VII lists the binary and ternary invariants of the system.

TABLE VII.- BINARY AND TERNARY INVARIANTS OF THE SYSTEM CAESIUM IODIDE–IODINE–WATER AT 740–750 mm.

Position	Temp. °C.	Liquid		Phases Present
		%I	%CsI	
S	0*E*	Trace	0	Ice, iodine, liquid
A	−4·0*E*	0	27·5	Ice, CsI, liquid
E	71·5*E*	81·2	18·8	Iodine, CsI_4, liquid
D	140 *U*	69·5	30·5	CsI_4, CsI_3, liquid
C	211 *U*	51·7	48·3	CsI_3, CsI, liquid
R	98·2*B*	0·4	0	Iodine, liquid, vapour
H	113*B*	99·9	0	Iodine, liquid, vapour
M	108·6*B*	0	71·4	CsI, liquid, vapour
N	303*B*	50·0	50·0	CsI, liquid, vapour
B	−4·0*E*	0	27·8	Ice, CsI, CsI_3, liquid
K	−0·5 *U*	0·3	3·5	Ice, CsI_3, CsI_4, liquid
L	−0·2 *U*	0·3	0·8	Ice, CsI_4, iodine, liquid
$\{F_1$	51·5	4·1	6·9$\}$	CsI_4, iodine, 2 liquids
F_2	51·5	74·3	23·2	CsI_4, iodine, 2 liquids
$\{G_1$	98·2 + *B*	3·8	4·6$\}$	Iodine, 2 liquids, vapour
G_2	98·2 + *B*	87·8	10·8	Iodine, 2 liquids, vapour
Q	109·6*B*	20·8	61·9	CsI, CsI_3, liquid, vapour
U	Unknown *B*	Unknown	Unknown	CsI, CsI_3, liquid, vapour

TEMPS: *E* = Eutectic pt.; *U* = Transition pt.; *B* = Boiling pt.. (740–750 mm.).

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SECTION XC

CAESIUM SULPHIDE

By L. F. WILSON

Cæsium monosulphide, Cs_2S, is prepared in the solid state by direct combination of the elements or by the reaction of cæsium metal with mercuric sulphide.[1] Combination of the elements in liquid ammonia is not suitable for this preparation.[2] An aqueous solution of the salt is made by saturating a solution of cæsium hydroxide with hydrogen sulphide and then adding the same quantity of cæsium hydroxide.[3] When prepared in an inert atmosphere the solution is colourless but hydrolysis and oxidation can produce free sulphur which colours the solution yellow. Cæsium monosulphide is a hygroscopic, white solid which reacts violently with water. The compound melts, with decomposition, at 510–520°C.[1] The magnetic susceptibility at −183°C. and 20°C. is $-0{\cdot}35 \times 10^{-6}$.

Cæsium hydrosulphide, CsSH, is prepared by methods analogous to those used for the preparation of rubidium hydrosulphide.[3] The compound crystallises in the cubic system, $a = 4{\cdot}29$ A., and has the cæsium chloride type structure.[3] The *X*-ray pattern remains unchanged after heating the hydrosulphide to 200°C.

Cæsium polysulphides up to the composition Cs_2S_6 are known. The colours of these polysulphides and their magnetic susceptibilities at −183°C. and 20°C. are given in Table I.[2]

TABLE I.- MAGNETIC SUSCEPTIBILITY OF CAESIUM SULPHIDES

Sulphide	Colour	Magnetic Susceptibility	
		at −183°C.	at 20°C.
Cs_2S_2	Yellow	$-0{\cdot}35 \times 10^{-6}$	$-0{\cdot}35_5 \times 10^{-6}$
Cs_2S_3	Red	$-0{\cdot}35 \times 10^{-6}$	$-0{\cdot}35_5 \times 10^{-6}$
Cs_2S_4	Dark red	$-0{\cdot}34_5 \times 10^{-6}$	$-0{\cdot}35_5 \times 10^{-6}$
Cs_2S_5	Dark red	$-0{\cdot}35 \times 10^{-6}$	$-0{\cdot}35_5 \times 10^{-6}$
Cs_2S_6	Brown	$-0{\cdot}35 \times 10^{-6}$	$-0{\cdot}35_5 \times 10^{-6}$

The potentiometric titration of cæsium polysulphide with cæsium metal in liquid ammonia solution, shown in Fig. 1, indicates the successive formation of the tetrasulphide and the disulphide.

Cæsium pentasulphide is prepared from a solution of the monosulphide and free sulphur. A deep-red colour develops on boiling the solution and large coral red crystals are deposited when the solution is evaporated in vacuo.[5] After drying in vacuo at room temperature cæsium pentasulphide monohydrate is obtained. The compound forms red, triclinic prisms with well developed faces; the crystal system is triclinic and the unit cell dimensions are:

$$a = 6{\cdot}91\text{ A.},\ b = 7{\cdot}81\text{ A.},\text{ and } c = 10{\cdot}44\text{ A.}$$
$$\alpha = 103^\circ\ 32',\ \beta = 108^\circ\ 10',\text{ and } \gamma = 97^\circ\ 50'.$$

The space-group is $P\bar{1}$ and the measured density, 2·94, corresponds to two

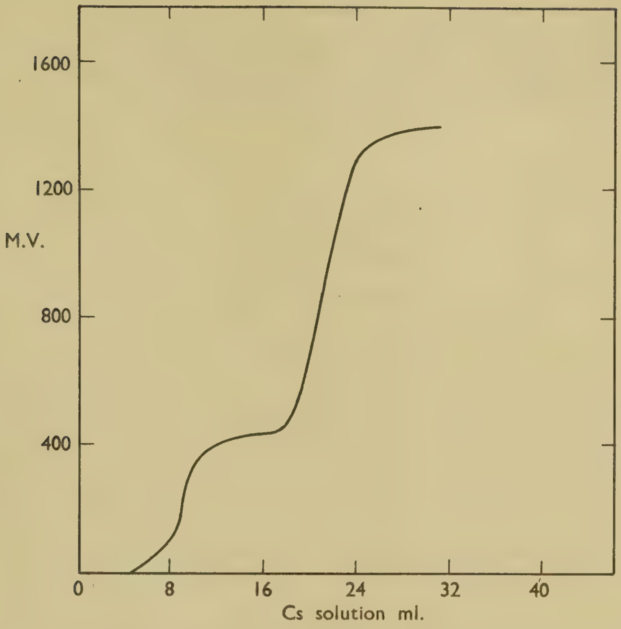

FIG. 1.- TITRATION OF CAESIUM POLYSULPHIDE WITH CAESIUM

molecules in the unit cell.

Anhydrous cæsium pentasulphide is prepared by dehydration of the monohydrate in vacuo for 10hr. at 80°C. At this temperature no loss of sulphur occurs. The anhydrous salt has m.p. 210°C. and *d* 2·94. It is a coral red powder and the *X*-ray diffraction pattern is markedly similar to that of the monohydrate.

Cæsium hexasulphide, Cs_2S_6, is prepared in the form of brown, prismatic needles by disproportionation of cæsium pentasulphide in 70% aqueous alcohol. The production of the hexasulphide indicates that in pentasulphide solutions $S_6^=$ ions are present in equilibrium with $S_5^=$ ions. The equilibrium is displaced in the direction of hexasulphide formation by the conditions in the aqueous alcohol solution.[5] The crystals of cæsium hexasulphide smell strongly of hydrogen sulphide and oxidise rapidly in air to give cæsium thiosulphate and sulphur. The compound crystallises in the triclinic system[6] and the unit cell dimensions are:

$$a = 11{\cdot}53\,\text{A.},\ b = 9{\cdot}18\,\text{A.},\ c = 4{\cdot}67\,\text{A.}$$
$$\alpha = 98^\circ\,13',\ \beta = 95^\circ\,12',\ \gamma = 95^\circ\,8'.$$

The space group is $P\bar{1}$ and the measured density, 3·076, indicates that there are two molecules in the unit cell. The structure of cæsium hexasulphide has been completely determined. The cæsium atoms are ionised and the resulting hexasulphide ion is non-branched and non-planar. The average S–S–S bond angle is 108° 8′. Two types of S–S bond, of length 2·02 A. and 2·11 A., arranged alternately along the sulphur chain, are present.

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SECTION XCI

CAESIUM SULPHATE

By N. M. HOPKIN

Physical Properties

The solubility[1,2] of caesium sulphate in *iso*propyl, propyl, ethyl, methyl, and *tert.*-butyl alcohols, dioxan, acetone and ethylene glycol and their mixtures with water at 25°C. exhibits a diminution with an increase in the concentration of the organic solvent. Taking the series in the order given, the preceding solvent decreases the solubility of caesium sulphate to a greater degree than the succeeding one for the same concentration. The log of the solubility (S) of caesium sulphate in methyl and ethyl alcohols and their mixtures with water varies in the inverse proportion to the dielectric constant (D) of the solvent at that concentration: $\log S = K + (A/D)$.

In the case of ethylene glycol the same relation is expressed by two straight lines: one for a mixture rich and one for one poor in water. The values of K, $-A$ and the concentration of the organic solvent for which this linear dependence holds true are for methyl alcohol, 4·25, 157·0 and 0–100% by wt., and for ethylene glycol 4·32, 158·4 and up to 85% by wt.

The integral heat of dilution (V_m) and the differential heat of dilution[3] (Φ_m) for caesium sulphate over the range 10^{-1} to 10^{-4} M. are shown in Fig. 1. At the highest dilution the latter is positive, rising to a maximum when the concentration is still small, but ultimately becoming negative.

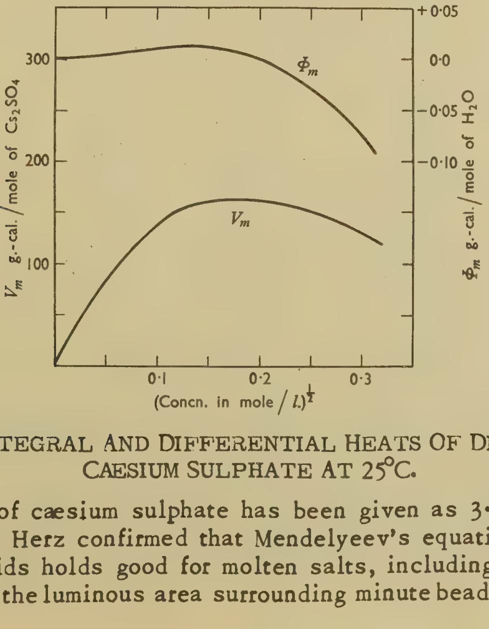

FIG. 1.- INTEGRAL AND DIFFERENTIAL HEATS OF DILUTION OF CAESIUM SULPHATE AT 25°C.

The density[4] of caesium sulphate has been given as 3·034 at 1040°C. and 2·890 at 1220°C. Herz confirmed that Mendelyeev's equations for the thermal expansion of liquids holds good for molten salts, including caesium sulphate.

Photographs of the luminous area surrounding minute beads of molten caesium sulphate on loops of platinum wire in the flame of a Méker type gas burner were used to determine the coefficients of diffusion[5] of cæsium in the flame. The border of the luminous area represents a uniform salt concentration of minimum visibility and corresponds to the equation:

$$K = (nv/2)[(dx/dn) - 1]$$

where K = coefficient of diffusion; n = distance of border of the flame to the bead; x = vertical distance of this point on the border above the head; v = vertical velocity of the flame gases.

For cæsium sulphate $K = 8{\cdot}5 \pm 10\%$. This result indicates that metal ions are free part of the time during diffusion and combined part of the time. The flame temperature was 1436°C.

A specimen of cæsium sulphate at 1200°C. in a stream of water vapour flowing at 18 g./hr. in a 20 mm. tube was found to lose 90·85% of its wt. in 1 hr. by simple volatilisation;[6] the molecular volatilities at this temperature of the sulphates of potassium, rubidium and cæsium are as 1·4:2·1:1, in spite of the closeness of their m.ps. (1074°, 1074° and 1019°C.). It would seem that volatility is determined less by the ionic bonding in the solid state than by the changes of bonding that take place after fusion. Stronger bonding in the solid state may give rise to a weakening in the liquid state.

The crystal structure[7] of cæsium sulphate is agreed by most workers to be a simple orthorhombic lattice containing 4 molecules per unit cell, for which $a = 6{\cdot}24$, $b = 10{\cdot}92$ and $c = 8{\cdot}22$ A.

The diffusion coefficients[8] of cæsium sulphate in water at 25°C. have been determined by Harned *et al.* using the conductance method. They found very good agreement between the observed and calculated values. The sulphate used was prepared from the chloride, dissolved in water, and precipitated by adding a large excess of ethyl alcohol. It was further purified by recrystallisation from water. The spectrographic analysis gave <0·001% Na or Li, <0·01% Rb and the pH of a 0·01 M. solution was 6·0.

TABLE I.- DIFFUSION COEFFICIENTS OF DILUTE AQUEOUS CAESIUM SULPHATE SOLUTIONS AT 25°C.

C	Coefficient of Diffusion $D \times 10^5$	
	Observed	Calculated
nil	—	1·569
0·00096	1·490	1·490
0·00102	1·484	1·488
0·00112	1·489	1·485
0·00120	1·482	1·482
0·00150	1·470	1·475
0·00248	1·442	1·455
0·00251	1·441	1·454
0·00378	1·435	1·436
0·00468	1·419	1·426
0·00472	1·424	1·426

The solubilities[9] of cæsium sulphate at high temperatures and pressures in water and uranyl sulphate solution have been determined in sealed containers by Jones *et al.*; the results are given in Table II.

Throughout the experimental range cæsium sulphate showed a positive temperature coefficient and there was no tendency for the solutions to become supersaturated. No crystals reappeared in any of the solutions when heated to *ca.* 310°C. The presence of uranyl sulphate, unlike that of yttrium, lanthanum, cadmium or silver sulphate, decreases the solubility of the saturating species, and the solid phase separating with 1·348*m*. UO_2SO_4 may be a double salt.

TABLE II.- SOLUBILITY OF CAESIUM SULPHATE AT HIGH TEMPERATURES AND PRESSURES

t°C.	Wt.-% Cs_2SO_4 in water	*t*°C.	Wt.-% Cs_2SO_4 in 1·348*m*. UO_2SO_4	*t*°C.	Wt.-% Cs_2SO_4 in 0·1272*m*. UO_2SO_4
23	63·5	167·7	0·30	53·8	64·19
175	71·8	178·5	0·33	61·6	66·00
211	73·5	187·3	0·37	77·3	67·12
270	75·0	214·8	0·44	84·2	67·55
292	75·5	245·3	0·49	104·8	68·58
		285·6	0·54	140·2	70·07
		288·6	0·78	177·5	71·66
				228·6	73·48

The cæsium sulphate–cæsium fluoride equilibrium diagram[10] is similar to that of rubidium sulphate–rubidium fluoride (Fig. 2). Both cæsium and rubidium form compounds of the general formula M_2SO_4,MF. The isotherms at 25°C. for the system cerium sulphate–cæsium sulphate–water[11] have been determined and the compound $Ce_2(SO_4)_3,Cs_2SO_4,8H_2O$ identified. It is a white crystalline powder with a pinacoid structure, {010}.

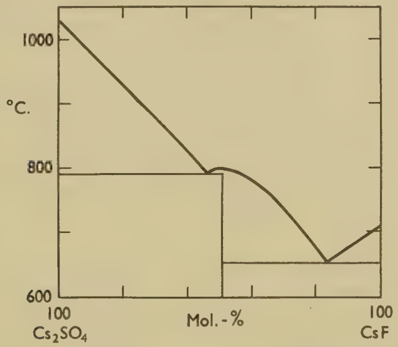

FIG. 2.- EQUILIBRIUM DIAGRAM OF THE CAESIUM SULPHATE–CAESIUM FLUORIDE SYSTEM

The system ammonium sulphate–cæsium sulphate in water[12] forms a continuous series of solid solutions with a congruent crystallisation point at 0·49 mole fraction of ammonium sulphate. Fig. 3 shows the distribution of ammonium sulphate between the liquid and solid phases in this system where y, the mole fraction of the ammonium sulphate in the dissolved salts, is plotted against its mole fraction in the solid solution (x).

The system cæsium sulphate–magnesium sulphate[13] has been studied by means of heating–cooling curves. Very pure cæsium sulphate was prepared by treating a solution of cæsium chloride with excess of sulphuric acid, neutralising with cæsium carbonate, evaporating to dryness and calcining. The liquidus of the system exhibits a slight inflexion at 63mol.-% $MgSO_4$, which indicates the formation of the compound $Cs_2SO_4,3MgSO_4$ (I) m.p. 835°C. There is a eutectic at 680°C. of α-Cs_2SO_4 with (I), corresponding to 45mol.-% $MgSO_4$.

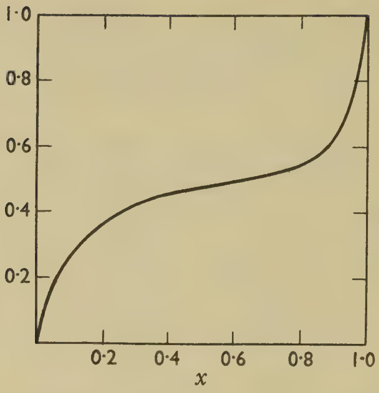

FIG. 3.- DISTRIBUTION OF AMMONIUM SULPHATE BETWEEN LIQUID AND SOLID SOLUTION IN THE SYSTEM $(NH_4)_2SO_4$–Cs_2SO_4–H_2O

In the solidus the compound $2Cs_2SO_4,MgSO_4$ was detected and was confirmed by *X*-ray analysis at 570°C., corresponding to 33·3mol.-% $MgSO_4$. In the binary system caesium chloride–caesium sulphate[14] there is a eutectic point at 553°C. corresponding to 29mol.-% Cs_2SO_4 and a transition point at 760°C. with 76mol.-% Cs_2SO_4 which corresponds to the polymorphous transition of the caesium sulphate. In the lithium sulphate–caesium sulphate system there are two congruent compounds. These are Li_2SO_4,Cs_2SO_4 (m.p. 738°C.) and $4Li_2SO_4,Cs_2SO_4$ (m.p. 637°C.). The first compound was obtained by crystallisation from the aqueous solution. Eutectic points lie at 680°C. with 31 mol.-% Li_2SO_4, at 630°C. with 75·5mol.-% Li_2SO_4 and at 620°C. with 89·2mol.-% Li_2SO_4. The two diagonal systems caesium chloride, lithium sulphate and lithium chloride, caesium sulphate are unstable. The diagonal Cs_2Cl_2–Li_2SO_4 intersects the crystallisation fields Cs_2Cl_2, Li_2SO_4,Cs_2SO_4, $4Li_2SO_4,Cs_2SO_4$ and Li_2SO_4. The analogous diagonal of Li_2Cl_2–Cs_2SO_4 also intersects the crystallisation fields of the two compounds and Li_2Cl_2, Li_2SO_4 and Cs_2SO_4. The liquidus curve consists of five branches intersecting at 432°, 457°, 470°, 610° and 624°C.

From the silver sulphate–caesium sulphate–water system[15] the only solid phases to be observed were the pure salts. Isothermally invariant solutions saturated with the two salts have the following compositions: at 25°C., 1·57% Ag_2SO_4, and 63·76% Cs_2SO_4, and at 35°C., 1·80% Ag_2SO_4 and 64·27% Cs_2SO_4.

Caesium and calcium sulphates together form a compound of the langbeinite type[26] $[A^I_2B^{II}_2(SO_4)_3]$, which is $Cs_2Ca_2(SO_4)_3$. Its density is 3·415 and its *a*-axis is 10·724 A.

The effect of caesium ions on the electrodeposition of copper[17] from sulphate solutions is to cause phase polarisation and to hinder the access of copper ions to the cathode. The phase polarisation occurs with 0·1 M. $CuSO_4$ + x M. Cs_2SO_4 up to $x = 0{\cdot}1$. The depressing effect of this polarisation increases from Li<Na<K<Rb<Cs. When $x = 0{\cdot}5$, $\Delta E = 0{\cdot}1$ V., and the activity energy is almost 8000 g.-cal. It is less at smaller values of x, but never less than 4500 g.-cal.

The entropy of fusion[18] of compounds decreases with decreasing ionic radius. This is attributed to the greater freedom of the tetrahedral SO_4^{2-} in the liquid than in the crystalline state, owing to the formation of voids. The rotation and vibration–liberation motion are more hindered in crystals containing large cations. Caesium sulphate, which melts at 1277°C., has a latent heat of fusion 9577 g.-cal.-mol., an entropy of fusion [S_f] 5·0 entropy units.

The ionic radius of the Cs^+ cation is 1·69A. The freezing points of solution of caesium sulphate[19] in sulphuric acid have been calculated from osmotic coefficients fitted to an extended form of the Debye–Hückel equation; the dielectric constant at 10°C. was taken as 115. The results are given in Table III, where the f.p. of sulphuric acid is taken to be 10·365°C.

TABLE III.-FREEZING POINT OF CÆSIUM SULPHATE IN SULPHURIC ACID SOLUTIONS

M. Cs_2SO_4	Freezing Point °C.
0·01	10·205
0·02	9·995
0·03	9·764
0·04	9·526
0·05	9·286
0·06	9·043
0·07	8·800
0·08	8·558
0·09	8·311
0·10	8·060
0·11	7·805

The activity (γ) and osmotic (ϕ) coefficients of cæsium sulphate have been accurately determined by the use of isopiestic methods.[20] The results are given in Table IV. These have been redetermined[21] very accurately by Stokes *et al.* These latest values may be arrived at by multiplying the activity coefficients (γ) in Table IV by 1·018.

TABLE IV.- OSMOTIC COEFFICIENTS AND ACTIVITY COEFFICIENTS OF CÆSIUM SULPHATE IN AQUEOUS SOLUTIONS

M.	Osmotic coefficient ϕ	Activity Coefficient γ
0·1	0·802	0·456
0·2	0·772	0·382
0·3	0·751	0·338
0·4	0·739	0·331
0·5	0·731	0·291
0·6	0·725	0·274
0·7	0·721	0·262
0·8	0·717	0·251
0·9	0·714	0·242
1·0	0·712	0·235
1·2	0·711	0·222
1·4	0·713	0·214
1·6	0·716	0·207
1·8	0·722	0·201

Chemical Properties

The temperatures in air within which cæsium sulphate[22] is stable were found to be 105–876°C. This study was made by means of Chevenard's[23] thermobalance. Later Hegedüs[24] used the same method to investigate the thermal decomposition of the sulphate and found the cæsium sulphate to be stable in air at atmospheric pressure up to 960°C. In a 30/70 hydrogen–nitrogen mixture flowing at 33l. per hr., cæsium hydrogen sulphate is converted into the normal cæsium sulphate at 300°C.; this is reduced at 620°C. to cæsium sulphide which volatilises at approximately 700°C. The reduction of the normal sulphate also starts in hydrogen[25] alone at 620°C., but in ammonia there is no sign of reduction by loss of weight until 770°C.

The reactivity of boron trifluoride[26] with the alkali-metal sulphates increases with increase of their atomic weight. Thus lithium sulphate will absorb only about 0·1 mol. of boron trifluoride, whereas cæsium sulphate will absorb 2 mols. to form the compound $Cs_2SO_4,2BF_3$.

High-temperature ion-exchange reactions result in the formation of lithium sulphate when β-spodumene[27] is calcined with cæsium sulphate at temperatures up to 1500°C. Although the reaction proceeds the more rapidly the higher is the temperature, it is slowed down and finally stops if the temperature is high enough to form a viscous glass.

The role played by alkali-metal sulphates in the catalytic oxidation of sulphur dioxide to sulphur trioxide has been much studied because of its industrial importance. Tandy[28] found that when vanadium oxide catalysts are used, in the temperature range 440–600°C., a liquid is formed consisting of vanadium compounds dissolved in an alkali-metal pyrosulphate–sulphate mixture. The m.p. of this mixture decreases with increasing at. wt. of the alkali metal forming the sulphate. The increase in weight observed with an alkali-metal sulphate/V_2O_5 mole ratio of 2·5/1 suggests the formation of normal pyrosulphate ($M_2S_2O_7$) and $VOSO_4$. When a cæsium sulphate/vanadium oxide mixture is used there is also evidence for the partial formation of a higher sulphate such as $M_2S_3O_{10}$. The extent of the reduction of the vanadium oxide is lower in the presence of the alkali metals of the higher at. wts. It is constant for cæsium sulphate between 410 and 520°C. The cæsium sulphate/vanadium oxide mixture can absorb more sulphur trioxide than would correspond to the formation of $M_2S_2O_7$ and $VOSO_4$ in the temperature range 380–470°C. At 400°C. 99·6% of the sulphur dioxide is converted to sulphur trioxide in a gas mixture containing 5% of sulphur dioxide, 20% of oxygen and 75% of nitrogen. *X*-Ray diffraction data[29] show that at 450–500°C. compounds approximating to the composition V_2O_5,Cs_2SO_4 are formed from mixtures of vanadium oxide and cæsium sulphate. When this preparation is mixed with silica to give a vanadium content of 6% its oxidation rate for sulphur dioxide at 420°C. is nine times that of the corresponding potassium preparation. The activation energy is 80 and 40 kg.-cal./mole in the lower and higher temperature ranges, respectively.

A "quick fusion" method[30] has been used to establish the conditions whereby normal alkali-metal sulphates are converted to the pyrosulphate by sulphur dioxide at atmospheric pressures. Cæsium pyrosulphate is formed at 400°C. This is the only alkali-metal pyrosulphate which is formed under conditions such that any appreciable decomposition has not begun. In most other cases the pyrosulphate reaction takes place 30–130°C. above its m.p. and 50–130°C. above the temperature at which its own decomposition starts. By the use of radioactive tracer techniques it was found that cæsium sulphate reacts with sulphur trioxide to form a polysulphate ($Cs_2SO_4,4SO_3$) between 20 and 100°C. No such polysulphates are formed under these conditions with lithium or sodium sulphates, although lower polysulphates are formed under these conditions with potassium and rubidium sulphates. The simplest cæsium polysulphate is $Cs_2SO_4,2SO_3$, which is stable between 160° and 300°C. The temperatures at which decomposition begins increase in the order of increasing at. wt.: $K < Rb < Cs$.

In their study of the reciprocal systems between cæsium chloride, potassium sulphate and cæsium sulphate, potassium chloride[31] Bergman *et al.* determined a deep minimum on the eutectic line and some shift of the reaction of decomposition towards the more stable diagonal pair – cæsium chloride, potassium sulphate because they possess a lower isomorphism than the corresponding potassium–rubidium system. This is shown by a corresponding curvature on the isotherms of the plane of isomorphous sulphate. Such a curvature is not observed in the potassium–rubidium system.

Biological

Caesium sulphate produces the same malformation[32] of *Salmonella paratyphi B* as is produced by the chloride and nitrate. The effect is dependent upon the cation, its concentration, the pH and the size of the inoculum. The caesium salt inhibits the oxidation actions of: *S. paratyphi-A*, and *-B*, *S. typhosa*, *Shigella*, *Escherichia coli*, *Aerogenes*, *Klebsiella* and staphylococci, but not of enterococci.

The formation of extreme growth forms in neutral media containing salts is closely related to their concentrations. Strains adapted to the abnormal concentration of salts develop faster, and form morphologically normal cells in media containing the salt. The adaptation is much faster to the highly toxic[33] caesium sulphate than to the less toxic sodium chloride.

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SECTION XCII

CAESIUM CARBONATE

By N.M. HOPKIN

Physical properties

The dielectric constant of cæsium carbonate, determined by Schupp,[1] is 6·53 (wave-length 1800m. at 18°C.). The use of powdered or fused salt does not give very reliable results, but Schupp devised a method whereby the powder is added to a liquid placed between the plates of a condenser, the liquid being changed until one is found whose total capacity is not changed by addition of the salt. The dielectric constant of the salt is then that of the liquid used. For example the dielectric constants of toluene, chlorobenzene and *o*-nitrotoluene being 2·31, 5·18 and 26·7 respectively, mixtures of these liquids can be used for such determinations.

Four- and five-liquid equilibrium systems, of which one of the phases can be a saturated solution of cæsium carbonate, have been reported by Carrière.[2] In the four-liquid system the other three liquids can be saturated ammonia in water, a saturated aqueous solution of sodium oleate and aniline, hexane, nitrobenzene, neutral peanut (or olive) oil or castor oil. An example of a five-liquid equilibrium system is saturated cæsium carbonate, a saturated aqueous solution of ammonia, concentrated sodium oleate solution, hexane and aniline. The volume of the sodium oleate phase decreases with increasing temperature and disappears altogether at 26°C.

Diogenov[3] has devised a classification system in order to study the trends of the thermal effects Q(kg.-cal./mole) of reciprocal systems formed by a pair of alkali metal ions and pairs of anions. In this he grouped together lithium-sodium, lithium-potassium, lithium-rubidium, lithium-cæsium and called it Group I, then for Group II sodium-potassium .....etc. making four Groups in all. Taking each Group separately, and independently of the nature of the anion pair, the systems are invariably irreversibly reciprocal, and for any given pair of cations and one fixed anion the shift of equilibrium is always the greater the smaller is the radius of the other anion of the pair. Taking one fixed cation (cæsium) for the systems containing hydroxyl and carbonate anions, then Q will increase with increasing atomic weight of the other cation (Table I.).

TABLE I.- THERMAL EFFECTS OF ALKALI METAL PAIRS WITH OH^- AND CO_3^{--} ANIONS

Alkali metal pairs	Q kg.-cal./mole
Li, Cs	0·3
Na, Cs	0·7
K, Cs	2·8
Rb, Cs	7·1

The equilibrium phase diagram for the binary mixtures of cæsium carbonate and caesium fluoride, given by Schmitz-Dumont and Heckman[4] is a simple eutectic system (Fig. 1.). The eutectic contains 43mole % of caesium carbonate and melts at 530°C.

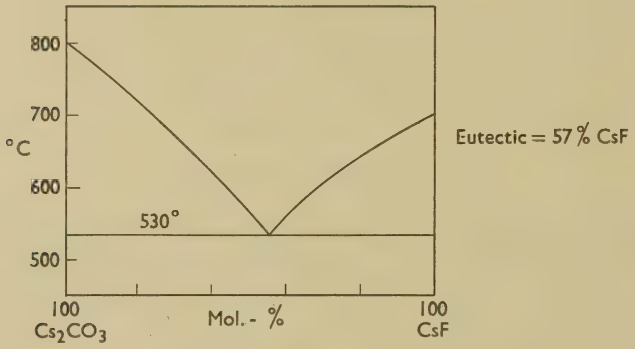

FIG. 1. EQUILIBRIUM DIAGRAM OF CÆSIUM CARBONATE AND CÆSIUM FLUORIDE

Formation and chemical properties

Cæsium carbonate[5] can be prepared by the action of carbon monoxide on cæsium hydroxide at temperatures above 300°C. At this temperature cæsium oxalate and formate will be formed to the extent of 91·5% of the latter. However, cæsium formate[6] behaves in the same manner as do potassium and sodium formates from the point of view of thermal and catalytic decomposition; cæsium carbonate is the principal product. In the presence of metallic sodium a yield of 84·9% of cæsium oxalate can be obtained at 300°C.

In his study of the hydrolysis of the alkali metal carbonates Guiter[7] has arrived at the following figures, taking the hydrolysis reaction in four stages:

(I) At about 1 N., $\Delta pH = 0{\cdot}05$

$$(CO_3^{--})_3 + 3H_2O \rightleftharpoons 3HCO_3^- + 3OH$$

No hydrolysis constant is given for cæsium but the percentage hydrolysis varies from 0·5 to 5·0%.

(I*a*) At about 0·1 N. there is a different reaction to the same point on the hydrolysis curve and $\Delta pH = 0{\cdot}3$.

$$CO_3^{--} + M^+ + H_2O \rightleftharpoons CO_3HM + OH$$

The hydrolysis constant here is $1{\cdot}58 \times 10^{-3}$ and equilibrium is reached at about 5%.

(II) At about 0·01 N., $\Delta pH = 0{\cdot}2$; the reaction becomes:

$$2CO_3^{--} + 2H_2O \rightleftharpoons (CO_3H^-)_2 + 2OH^-$$

The hydrolysis constant is now $3{\cdot}5 \times 10^{-6}$ and the hydrolysis increases from 5% to 15%.

(III) At about 0·001 N., $\Delta pH = 0{\cdot}75$; the hydrolysis equation is as follows:

$$CO_3^{--} + 4M^+ + H_2O \rightleftharpoons (CO_3M_4H)^{+++} + OH^-$$

The hydrolysis constant is now $4{\cdot}0 \times 10^{-5}$ and the hydrolysis decreases from

15% to 0·2%.

(IV) At about 0·0001 N., ΔpH = 0·15;

$$CO_3^{--} + H_2O \rightleftharpoons CO_3H^- + OH^-$$

The hydrolysis constant is now $5·0 \times 10^{-10}$ and the hydrolysis increases again from 0·2% to 0·5%. The hydrolysis reactions are identical for sodium, potassium and lithium as well as for caesium and rubidium when the metals do not enter into the reaction. In a 0·001 N. solution cation complexes appear, the structures of which point to the existence of steric hindrance.

When anhydrous neutral caesium carbonate[8] is added to an aqueous solution of ammonia of any concentration and the temperature of the mixture is kept below 20°C., two layers will form when the saturation point is reached. The upper layer will contain 99% of the ammonia and the lower layer 99% of the carbonate. These layers are stable in the presence of potassium hydroxide and orthophosphoric acid, but they become completely miscible upon dilution or when heated above 60°C. Copper acetate added to this system will dissolve and become concentrated in the lower layer, and only traces of the copper will be found in the upper layer. If the carbonate layer is not saturated the addition of the copper salt will cause the layers to coalesce. But on adding more carbonate to the point of saturation, the two components will again separate and the copper will be found in the lower layer of the system.

The reactivity[9] of titanium oxide with the alkali carbonates decreases in the order: caesium (decomp. 610°C.), lithium (m.p. 732°C.), rubidium (m.p. 837°C.), sodium (m.p. 852°C.), and potassium (m.p. 891°C.), which is the same order as that of their melting points.

While studying the thermodynamic properties of carbonates in order to elucidate their behaviour in metallurgical processes, Kelley and Anderson[10] have assembled what data exist on caesium carbonate. Lebeau's[11] results refer to the liquid state (883°–1453°K.) and the following dissociation pressure equation represents his results:

$$Cs_2CO_3 \rightarrow Cs_2O + CO_2$$

$$\log_{10}P(\text{atm.}) = \frac{6080}{T} + 3·532$$

$$P_{CO_2} = 1 \text{ atm. at } 1720°\text{C.}$$

De Forcrand[8] has given 97,530 g.-cal. as the heat of dissociation of caesium carbonate at room temperature and Rengade[12] reported –82,700 g.-cal. for the heat of formation of the oxide. From these figures and from the heat of formation of carbon dioxide the heat of formation of the carbonate may be computed:

$$2Cs + C(\beta\text{-graphite}) + \tfrac{3}{2}O_2 = Cs_2CO_3$$

$$\Delta H_{291} = -274,470 \text{ g.-cal.}$$

Applications

Caesium carbonate, when used as a condensing agent[13] in the transformation of *o*-aroyloxyacetarones into *o*-hydroxydiaroylmethanes, gives a yield of 75%.

In studying the upward movement of water and salt solutions in the black cotton soils of India, Ramdas and Mallik[14] found that a 2% solution of the alkali metal carbonates caused rapid swelling of the soil particles, but the swelling was in inverse proportion to the weight of the metallic radical of the salt. No swelling occurred if the soil was first subjected to prolonged

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heating, which indicated that this effect was due to the colloidal coating of the particles.

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SECTION XCIII

CAESIUM NITRATE

By N. M. HOPKIN

The solubility of caesium nitrate in water, heavy water and in light and heavy water mixtures at 5°C. is shown in Table I according to the findings of Noonan.[1] This difference in solubility is of the same order as for silver chlorate, thallous perchlorate, potassium permanganate, thallous nitrate, potassium perchlorate, silver cyanide, sodium oxalate and potassium silver cyanide at the same temperature. These differences of solubility in light and heavy water have been attributed[2] to the persistence of the molecular association of deuterium oxide at high temperature, which would lower the solubility of the salts in it.

TABLE I.- SOLUBILITY OF CAESIUM NITRATE IN LIGHT AND HEAVY WATER MIXTURES

Solubility in Moles of Salt per Moles of Solvent				
H_2O	91·43% D_2O	Observed difference	Extrapolated[3] diff. for pure D_2O	Difference %
1·078	0·9056	0·172	0·188	17·4

The difference figure in column 4 of Table I was found by linear extrapolation from the solubility figures for pure water and for 91·43% deuterium oxide. This was assumed to be justified because Lange and Martin[3] found that the difference in the integral heat of solution of sodium chloride in water and water–deuterium oxide mixtures was a linear function of the deuterium content of the water when the concentration was expressed in moles of salt per 100 moles of water.

The solubility of lead nitrate is increased[4] in aqueous solution by the presence of caesium nitrate. Fig. 1 shows this influence and that of other alkali metal nitrates. Their influence on the solubility of lead nitrate increases in the order Li < Na < K < Cs, which is the same as that of their ionic radii, which are 0·60, 0·95, 1·33 and 1·69 A. respectively. Hydration of the alkali metal ions varies inversely with the ionic radii, so that the more water held by each ion the smaller is the solubility of the lead nitrate, as shown in Fig. 1. The formation of complexes opposes the influence of hydration and this tendency increases from lithium to caesium, which fact also confirms these observed solubilities. The influence of cation radius and salt concentration upon the salting out of ethyl ether from aqueous nitrate solutions has been studied by Heal.[5] The solubility of ethyl ether in aqueous caesium nitrate solutions is shown in Table II, where the probable error for low values of m is ±0·03%.

The best equation to describe the effect of salt concentration is $\log S_0/S = km$, where S_0 and S are the molal solubilities of ethyl ether in pure water and in the solution of the salt of molality m respectively. At high concentration the salting-out is less than that predicted by the equation. The solubility (S_0) of ethyl ether in water was found to be 0·8599 molal. The effect of cation radii was again in the same direction as found for lead nitrate at low dilutions.

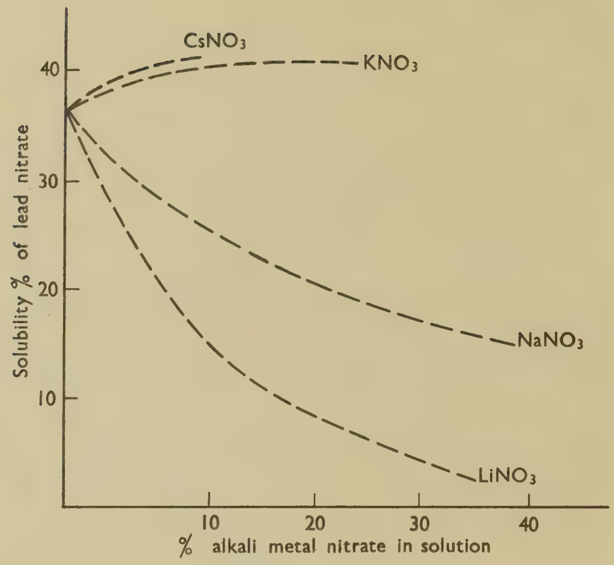

FIG. 1.- SOLUBILITY CURVES OF LEAD NITRATE IN SOLUTIONS OF ALKALI METAL NITRATES OF VARIOUS STRENGTHS

TABLE II.- MOLAL SOLUBILITIES OF ETHYL ETHER IN AQUEOUS CAESIUM NITRATE AT 25°C.

Solubility of Et_2O molality	Concentrate of $CsNO_3$ molality
0·8536	0·0250
0·8486	0·0514
0·8385	0·1003
0·8266	0·1503

The low melting points of the Group I nitrates as compared with the corresponding halides [cf. caesium nitrate, m.p. 414°C., caesium chloride, m.p. 646°C.] are attributed[6] to the formation of associated complexes. This process could contribute a term to the over-all entropy of fusion (S_f) without greatly increasing the heat of fusion (Hf). As the temperature of fusion

$$T_f = H_f/S_f$$

this would explain the unusually low melting-points. The small change in the volume on fusion of the nitrates and the abnormal activation energies for the viscosities of the molten nitrates support this suggested explanation.

The crystal lattice of cæsium nitrate between 161°C. and its melting point at 313°C. is cubic[7] with a lattice constant of 4·49 A. In this Finbak confirms the results of Gossner, Wallerant and Pauling and Sherman.[8] At lower temperatures the form is pseudocubic with the lattice constant ~4·45 A. Single crystals are not destroyed when heated from 15°C. to 200°C.; therefore the cæsium ions are very little altered in position during the transition at 161°C. It is difficult to determine the true symmetry of the crystals at low temperatures, but they closely resemble rubidium nitrate crystals which are orthorhombic. This makes an assumed hexagonal form probable with the likely space group of C_{3v}^2. This is contrary to the results reported by Waldbauer and McCann[9] who give the lattice constants of 10·74 and 7·68A. for the axes *a* and *c* respectively and could find no evidence for the transition at 161°C. However Korhonen[10] established the cubic structure of cæsium nitrate above 161°C. His samples were in the form of pressed briquettes in a glass mould and were held at 166–9°C. for 24 to 72hr. prior to grinding with benzene. The Wasastjerna photographic procedure was used to measure the *X*-ray intensities. NO_2 was assumed to be spherosymmetrical with N–O = 1·22A. The O and N atom parameters were found to be $x = 0{\cdot}219 \pm 0{\cdot}008$, $y = 0{\cdot}219 \pm 0{\cdot}008$, $z = 0{\cdot}386 \pm 0{\cdot}002$ for O, and $u = 0{\cdot}275 \pm 0{\cdot}002$ for N. The temperature factor for cæsium at 167°C. corresponds to a r.m.s. displacement of 0·407A. These results disprove the hypothesis of a symmetrical rotation of the NO_3 group, although evidence[11] deduced from the variation of the mol. heat with temperature shows the possibility of free rotation taking place between 145°C. and 161°C. The mol. heats for cæsium nitrate can be expressed by the equation:

$$C_p = 9{\cdot}84 + 4{\cdot}64 \times 10^{-2}T$$

(between 273°K. and 373°K.). These temperatures are below the lowest hexagonal-to-cubic form transition points that accompany the onset of free rotation of the NO_3^- ion. The mol. heats between 0°–200°C. as determined by means of an ice-calorimeter are given in Table III.[11]

TABLE III.- MOLECULAR HEATS OF CAESIUM NITRATE

°C.	Mol. Heat
0	22·5
30·1	23·92
60·2	25·32
99·6	27·12
150·0	40·30
170·0	40·56
200·0	41·62

Investigation[12] of the system silver nitrate–cæsium nitrate from the evidence of heating and cooling curves has established the existence of two eutectic points at 168·5°C. and 163°C. where the silver nitrate content is 82·5% and 67·5% respectively. The liquidus curve exhibits a maximum at 171·5°C. (25% caesium nitrate); and at 173°C. (47·5% cæsium nitrate) there is a break beyond which the curve rises smoothly to the m.p. of cæsium nitrate. This is evidence for the existence of the compounds $AgNO_3,CsNO_3$ which is a vitreous mass, and the elongated prisms of $3AgNO_3,CsNO_3$. The latter exhibits a eutectic mixture with silver nitrate at 168·5°C. No solid solutions exist. The system $3AgNO_3,CsNO_3$–$CsNO_3$ contains the compound $AgNO_3,CsNO_3$ which decomposes above 173°C. Again solid solutions are absent. Palkin[12] has suggested the formula $Ag_2[Cs(NO_3)_3]$ for the double salt.

The equilibrium diagrams for the binary mixtures cæsium nitrate–lead nitrate and cæsium nitrate–lithium nitrate are both shown in Fig. 2. The former exhibits a eutectic at 176°C. with 32 mol.-% of lead nitrate. Pushin[13] did not carry this investigation beyond 50 mol.-% of lead nitrate. The eutectic mixture of the cæsium nitrate–lithium nitrate system occurs at 174°C. with 57 mol.-% of lithium nitrate. No solid solutions were found. In aqueous solution two compounds of cæsium nitrate and thorium nitrate have been estab-

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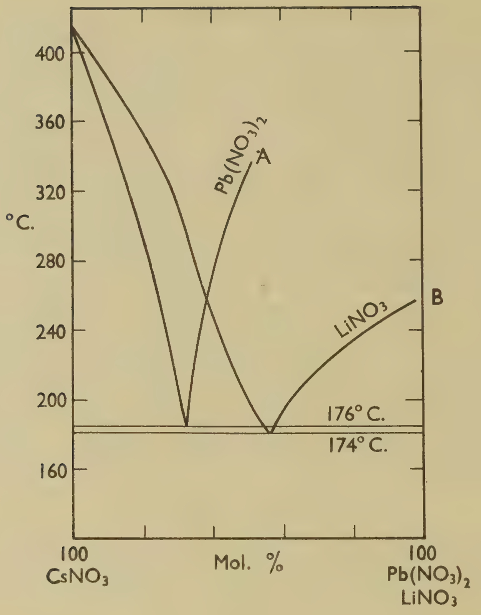

FIG. 2.- EQUILIBRIUM DIAGRAMS FOR THE CAESIUM NITRATE–LEAD NITRATE SYSTEM (A) AND THE CAESIUM NITRATE–LITHIUM NITRATE SYSTEM (B)

lished[14] by measurements of their heats of mixing. They are $9Th(NO_3)_4,7CsNO_3$ and $7Th(NO_3)_4,9CsNO_3$. The solid compound $Th(NO_3)_4,2CsNO_3$ could be isolated. The magnetic susceptibility $[\chi_M]$ for this compound has been determined $[\chi_M = -125{\cdot}3 \times 10^6]$, but this differs from the calculated value of -236×10^6, which indicates that there is some modification in the molecular structure. The thorium nitrate molecule is strongly attached to the caesium nitrate and the diamagnetism of the two constituents falls.

Hydrazine nitrate[15] forms a eutectic mixture at 43°C. with 36mol.-% of cæsium nitrate, but there is no evidence of any double salts. Reciprocal systems with a pair of alkali-metal cations and the anion pair of hydroxide and nitrate have been classified[16] into four groups with respect to the alkali metals. Thus Group 1 comprises metals adjacent in the periodic system, Group 2 comprises pairs of alternate alkali metals, Group 3 comprises the pairs Li–Rb and Na–Cs, whilst the fourth Group consists of the lithium–cæsium pair. The thermal effects, Q (kg.-cal./mole), of the exchange reactions of some of these systems is shown in Table IV.

TABLE IV.- THERMAL EFFECTS OF ALKALI METALS PAIRS WITH OH^- AND NO_3^- ANIONS

Alkali Metals Pairs	Q kg.-cal./mole
Li,Cs	3·0
Na,Cs	4·7
K,Cs	10·8
Rb,Cs	22·0

The thermal effect increases on descending Group 1 of the Periodic Table. The stable pairs of salts are always the hydroxides of the light metal with the nitrate of the heavier, e.g., cæsium nitrate with the hydroxides of the other alkali metals. Layering is absent with the cation pairs of cæsium and rubidium, but is present in the case of the cæsium cation and the rest of the alkali metals. In these hydroxide–nitrate systems there is a tendency for compounds of the type MOH,MNO_3 to occur where M is the same alkali metal. These can be considered as acid salts of orthonitric acid (H_3NO_4).

The caesium nitrate–caesium chloride equilibrium system[17] has a eutectic mixture, containing 69·6 mol.-% of the nitrate, which melts at 362°C. Mixtures of caesium nitrate and rubidium nitrate form a continuous series of solid solutions showing a shallow minimum on the melting curve at 290°C. Protsenko[18] has investigated the ternary system of the nitrates of cæsium, thallium and cadmium by determining melting points of two- and three- component mixtures. Cæsium and cadmium nitrates react in the liquid state to form the compound $Cd(NO_3)_2,2CsNO_3$, m.p. 178°C., and caesium and thallium nitrates give a continuous series of solid solutions. The ternary system has a nonvariant point of composition 31 mol.-% of thallium nitrate, 17·2 mol.-% of cæsium nitrate and 51·8 mol.-% of cadmium nitrate, m.p. 108°C.; and it has another with the composition of thallium nitrate 35·5 mol.-%, cæsium nitrate 16·1 mol.-% and cadmium nitrate 48·4 mol.-%, m.p. 84°C. The ternary system has four phases of crystallisation of which $Cd(NO_3)_2$ occupies 22·32%; an isomorphic mixture of caesium and thallium nitrates covers 66·68%, the compound $Cd(NO_3)_2,2CsNO_3$ 7·35% and $Cd(NO_3)_2,2TlNO_3$ 1·65% of the area of the ternary diagram of crystallisation. The mixtures show vitreous and supercooling properties. In the ternary mixtures of the nitrates of cæsium, rubidium and calcium the existence of the compound $Ca(NO_3)_2,CsNO_3$ has been confirmed.[19]

An interesting method at differential thermal analysis has been used by Gordon *et al.* to determine the melting points and temperatures of crystalline transitions. This method measures the temperature difference between an inert reference compound, such as ignited alumina, and the sample to be investigated, when they are heated together at a constant rate in the same furnace. The reference material chosen is one which will not undergo any thermal reactions over the temperature range to be used. Therefore any exo- or endo-thermic changes in the sample will cause its temperature to be higher or lower, respectively, than that of the reference material. These exo- or endo-thermic differentials can be recorded as a function of the temperature of the sample or of the furnace. This method has given the melting point of cæsium nitrate as 404°C. The compound bubbles slightly at 531°C., bubbles rapidly at 655°C. and vigorously at 850°C. Tzentnershver[21] gives 584°C. as its temperature of dissociation.

The heat of hydration $H^{\pm}$ (kg.-cal./mole), based on measurements of the heats of solution (L) at infinite or very high dilution and the value of lattice energy (U) has been given[22] as 136 for cæsium nitrate. The lattice energy values can be uncertain up to ±2% and this, on the average, will apply to the heats of hydration. Mishchenko's figures are more comprehensive than those of Bernal and Fowler and sometimes differ from them.

The practical osmotic and activity coefficients of cæsium nitrate over a wide range of concentrations have been determined by an isopiestic method.[23] This depends upon the difference in vapour pressure of two salt solutions. A small volume (2 ml.) of potassium chloride and the same volume of a solution of the salt to be studied are placed in two separate gold-plated platinum dishes in a desiccator which is evacuated, maintained at 25°C. and rocked gently. Distillation occurs until both solutions have attained the same vapour pressure. Equilibrium is reached in 24 hr. if the concentration of the solutions is at least 0·5 M. Changes in weight of the two solutions will give the isopiestic concentration. The errors in calculating osmotic pressure and activity coefficients are not greater than 0·3% at 0·005 mm. pressure of mercury for a 0·2 M. solution. Table V shows the activity coefficients for cæsium nitrate as calculated from freezing point data[24] for dilute aqueous solutions from concentrations of 0·001 M. to 0·01 M., and activity coefficients and osmotic pressures calculated from isopiestic[25] measurements for concentrations from 0·1 M. to 1·5 M.

TABLE V.- OSMOTIC AND ACTIVITY COEFFICIENTS OF AQUEOUS SOLUTIONS OF CAESIUM NITRATE

Solution Strength M.	Osmotic Coefficient ϕ	Activity Coefficient γ
0·001	–	0·966
0·005	–	0·928
0·010	–	0·902
0·1	0·902	0·726
0·5	0·804	0·524
1·0	0·736	0·417
1·5	0·685	0·353

The degree of dissociation (α) of cæsium nitrate calculated from conductivity data[26] in aqueous solutions of 0·05 M. and 0·1 M. has been given as 0·966 and 0·947 respectively. The corresponding dissociation constants (K) are 0·95 and 0·99, assuming that the activity of the undissociated portion of the salt is equal to its concentration, and that the mean activity coefficient of the ions is the same as in a potassium nitrate solution of the same strength. The ionization equilibrium constants[27] (K_1) of cæsium, rubidium and potassium nitrates are all 1·47. Caesium nitrate has the strongest association capacity of the three; the other two salts have equal capacities. There is no hydration of cæsium, rubidium, potassium and the nitrate ions at 100°C.

The thermal coefficient of expansion for molten cæsium nitrate is K = 0·0004073 (445°–575°C.). Herz's[28] figures for several compounds show that Mendelyeev's equations for the thermal expansion of liquids hold good for molten salts also.

The surface tensions of dilute aqueous solution of cæsium nitrate have been determined by a modified capillary-rise method,[29] the results being given in Table VI. At concentrations less than 0·01 M. the surface tension is less than that of pure water.

TABLE VI.- SURFACE TENSION OF AQUEOUS SOLUTIONS OF CAESIUM NITRATE

Solution Strength M.	Relative Surface Tension
0·0001	0·99992
0·001	0·99983
0·01	1·00013
0·1	1·00217

The diffusion coefficients (D) at 20°C. for cæsium nitrate[30] in aqueous solutions of normalities 0·1, 0·25 and 0·5 are 1·380, 1·354 and 1·322 respectively. The viscosity of aqueous solutions of cæsium nitrate has been determined accurately by Jones and Talley[31] using an Ostwald type viscometer and timing the rate of flow automatically by means of a photoelectric cell. The results shown in Table VII and Fig. 3 confirm the prediction of Jones and Dole,[32] based on

Debye's theory of interionic attraction, that all salts will be found to increase the viscosity of water if measured at sufficiently low concentration, including those salts which give a lower viscosity at moderate concentrations.

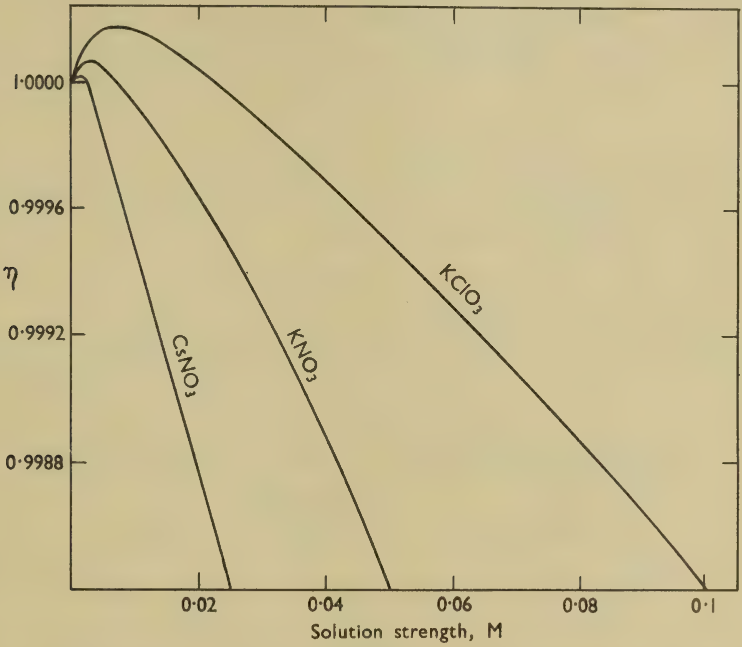

FIG. 3.- VISCOSITY OF AQUEOUS SOLUTIONS OF CAESIUM NITRATE, POTASSIUM NITRATE AND POTASSIUM CHLORATE

TABLE VII.- OBSERVED VISCOSITY OF AQUEOUS CAESIUM NITRATE SOLUTIONS

Solution Strength M.	Observed Viscosity centipoises η
0·0005	1·00003
0·001	1·00003
0·002	1·00000
0·005	0·99986
0·020	0·99876

The specific heat[32] of 210·01 g. of pure cæsium nitrate dissolved in 1375·2 g. of water is given as 0·8395 by Richards and Rowe. Table VIII shows the specific heat and heats of dilution of the nitrate.

TABLE VIII.- HEAT OF DILUTION AND SPECIFIC HEAT OF AQUEOUS CAESIUM NITRATE

Caesium Nitrate/Water Mixture	Heats of Dilution g.-cal.	Specific Heat
$CsNO_3$,$60H_2O$ + $40H_2O$	−293	0·8395
$CsNO_3$,$100H_2O$ + $100H_2O$	−260	0·8945
$CsNO_3$,$200H_2O$ + $200H_2O$	−150	0·9427

Refs. p. 2412

The molar energy of interaction[33] of ions of the nitrate in concentrated aqueous solutions is related to $\sqrt{C}$, where C = volume concentration of the solution of the electrolyte in g.-mol./l. of solution. The deviation of most strong electrolytes from this relation can be caused by the formation of liquid hydrates of ions of various stoicheiometric compounds that are able to dissociate in the solution. For aqueous solutions of cæsium nitrate at 25°C. the constants a and b are 0·122 and 1·078 respectively in the expression:

$$w = a + b\sqrt{C}$$

where w is the molar energy of interaction of the ions.

The electrical conductivity of molten cæsium nitrate has been accurately measured[34] over the temperature range 446·6°C. to 556·3°C. and the molecular conductivities calculated from the expression:

$$\mu_t = 42{\cdot}13 + 0{\cdot}120(t - 450)$$

show very good agreement with the observed values.

The electrical conductivity[35] of aqueous solutions of cæsium nitrate at various concentrations is given in Table IX for the temperatures 0°, 18° and 100°C.

TABLE IX.- CONDUCTIVITIES OF CAESIUM NITRATE AT VARIOUS CONCENTRATIONS AT 0°C., 18°C. AND 100°C.

Solution Strength M.	Conductivities		
	0°C.	18°C.	100°C.
0	84·4 ± 0·2	130·8 ± 0·3	389·5 ± 0·5
0·0005	83·1	128·6	383·0
0·001	82·5	127·6	379·5
0·002	80·3	123·8	367·5
0·01	78·6	121·3	359·0
0·02	76·5	118·1	347·5

Solid nitrates tend to decompose under the action of light. Doigan[36] has measured the rate of nitrite formation when crystalline cæsium nitrate is irradiated with light of wave-length 2000–3500A.

The approximate quantum yield is 0·19, in comparison with a quantum yield of 0·2 for formation of nitrite from nitrate solutions.

Applications — Biology

There is no appreciable chemotherapeutic activity of cæsium nitrate against typhus[37] in the guinea pig or the rat.

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SECTION XCIV

CÆSIUM PHOSPHATE

By N.M. HOPKIN

Physical Properties

No order-disorder type of transition has been observed with cæsium dihydrogen phosphate.[1] This may be due to the formation of a lattice like that of the metastable rubidium dihydrogen phosphate. The complex dielectric constant of the acid phosphate[2] changes rapidly at 165°K. and 9500Mc. which indicates a transformation of the second order, and this may also be ferroelectric.

Mixed crystals of potassium hydrogen phosphate with cæsium[3] ions show a lowering of the Curie point and of the maximum resonance temperature. The tetragonal crystals of cæsium dihydrogen phosphate[3] have been grown from a saturated solution and possess seignettoelectric properties in the direction of the *c* axis with a Curie point at about 159°K. Mixed crystals of cæsium and ammonium dihydrogen phosphates may be crystallised from aqueous phosphate solutions. These have piezoelectric properties[4] if the cæsium/ammonium ratio is not greater than 1·5. At higher ratios non-piezoelectric monoclinic crystals are precipitated. The presence of traces of barium and sulphate ions in cæsium dihydrogen phosphate[5] can change its electrical resistivity as their ionic radii are similar to that of the phosphate ion. Addition of 0·055% of silica as sodium silicate improved the resistivity. This is true for *P*-type crystals generally.

The following crystallographic data have been established by Corbridge[6] for the Kurrol salt of cæsium, $(CsPO_3)_n$: $a:b:c$ = 12·71:4·32:6·83 A.; β = 83°C.; mols/unit = 4; $d_{\text{calc.}}$ = 3·78 g./c.c.; space group = $P2_1/n$.

Chemical Properties

The decomposition of acid cæsium phosphate[7] has been studied by means of temperature-time curves which are obtained when heat is applied at a constant rate. Breaks in such curves show when endothermic reactions, such as the evolution of water or oxygen, occur. The temperature of decomposition was found to vary with the external pressure, and at a pressure of 710mm. of mercury the acid cæsium phosphate decomposes at 360°C.

When precipitated phosphates of iron and aluminium are digested in solutions of potassium or ammonium phosphate, potassium or ammonium ions are absorbed to form complex phosphates of the respective uni- and tri-valent cations; similar complexes[8] are formed when they are digested in cæsium phosphate solutions.

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SECTION XCV

THE SPECTROSCOPY OF CAESIUM AND CERTAIN OF ITS COMPOUNDS

By R. F. BARROW and LADY ANNE THORNE

THE SPECTRUM OF ATOMIC CAESIUM

By ANNE THORNE

General Discussion and Excitation of the Spectrum

Introduction.

The spectrum of atomic cæsium has been studied since the early days of spectroscopy and correlated with the spectra of the lighter alkali metals, which have played an important part in the development of modern spectroscopic theory. Brief historical accounts with references are given in many of the standard text-books on spectroscopy and in certain review articles.[1-3,9,13]

A description of the caesium spectrum and its explanation in terms of modern theory is also to be found in standard text-books.[1-6] The neutral cæsium atom has the ground state electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 6s\ {}^2S_{1/2}$, with the $6s$ electron outside a xenon-like core of closed shells, giving rise to a doublet spectrum. The first doublet of the principal series lies in the infra-red at 8521 A. and 8943 A. and the second and third in the violet and near ultra-violet at 4555 A., 4593 A. and 3876 A., 3888 A., respectively; the rest of the principal series is in the ultra-violet. The sharp, diffuse and fundamental series all have their first two or three terms in the infra-red and the remainder in the visible region. The most important energy levels and transitions of Cs I are shown diagrammatically by Grotrian.[7] Numerical values of experimentally determined energy levels of Cs I and II were tabulated in 1932 by Bacher and Goudsmit,[8] and brought up to date in 1958 by Moore.[45]

The first tabulations of line series for Cs I were given by Fowler[9] and Paschen–Götze[10] in 1922. The M.I.T. wave-length tables,[11] which list the arc and spark lines of all elements between 10,000 A. and 2000 A. in order of wave-length, include a list of the 'raies ultimes'; these are also given in the Vatican Observatory 'Atlas of Persistent Spectra'.[12]

In 1938 Shenstone[13] published a summary of spectroscopic work on the arc and spark spectra of all elements, incorporating tables showing how thoroughly each spectrum had been investigated. Meggers[14] brought the information up to date in 1946, and at the same time Hartree[15] presented in a similar way a summary of the calculations of wave functions and energy levels.

Excitation of the Spectrum.

The spectrum of atomic caesium has been excited in flames, arcs, sparks and various forms of discharge. Reference is here made only to those papers in which the conditions or mechanism of excitation have been the main consideration. Accounts of wave-length and intensity measurements and of specialized light sources for particular investigations are given later; in particular, references to spark sources are given in the sub-section on the spectrum of ionized caesium (see page 2421).

In flames several investigations have been made of the relation between the intensity of the spectral lines and the concentration of the caesium salts. This relation has generally been found to follow a linear law at low concentrations and a square-root law at higher concentrations.[16-18,41] The process of excitation appears to be thermal.[18,41] Different methods of introducing the salt into the flame have been described,[18,20] and the effect on the intensity of the caesium lines of adding other alkalis has been studied.[19]

In the electric furnace lines have been observed in emission as well as absorption.[21] Excitation by collisions with atoms of helium[23] and hydrogen[22,23] has been investigated.

In the caesium arc, studies have been made of the temperature distribution and electron density[24,25] and of the variation of intensity with concentration of the caesium salt solution.[26] Spark lines have been found in an interrupted arc.[27] A convenient lamp for excitation of the Cs I spectrum has been developed.[44]

In glow discharges passed through mercury vapour mixed with the vapour of caesium or of the other alkali metals, relative intensities have been measured.[28,29] The spectra of the cathode glow[30] and of the positive column[31] of glow discharges run in caesium vapour have been investigated, and experiments carried out on the electron voltage necessary for excitation,[32,33] and the electron density and distribution in a magnetic field.[42,43] The population of excited levels in the positive column has been measured by the line reversal method.[34-36] In electrodeless discharges in caesium vapour both the arc and the spark spectra are excited.[37-40]

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The Spectrum of Neutral Caesium

The ground state of the neutral caesium atom is $6s\ ^2S_{1/2}$, with a xenon-like core of closed shells. The ionization potential of 3·8926 V. corresponds to a term value for the ground state of 31,406·54 ± 0·03 cm.$^{-1}$.[10]

Term values of Cs I were tabulated in 1932 by Bacher and Goudsmit[1] from the tables of Fowler[2] and Paschen–Götze[3] with a few later additions.[4,5] Work done since 1932 covers some of the infra-red doublets,[6] and accurate interferometric measurements have been made on the second member of the principal series[7] and the first members of the fundamental.[8] In 1949, McNally *et al.*[9] and Kratz[10] both studied the principal series in absorption and measured respectively up to 62*p* (doublets resolved up to 14*p*)[9] and up to 73*p* (resolved up to 21*p*).[10] In Kratz's work the hyperfine structure of the ground state was resolved throughout. The series limit found by Kratz is 31,406·54 ± 0·03 cm.$^{-1}$ from the centroid of the ground state hyperfine structure (or 31,406·71 cm.$^{-1}$ from the lower of the two levels). Kratz ascribes the discrepancy of 0·22 cm.$^{-1}$ between his value for the series limit and that of McNally *et al.* (31,406·32 cm.$^{-1}$) to a pressure shift in the latter work. The Cs I term values derived from these sources, together with some unpublished material, are incorporated in Vol. III of the National Bureau of Standards 'Atomic Energy Levels', published in 1958.[86] Term values cover excited states of the 6*s* electron from 7*s* to 12*s*, 6*p* to 73*p*, 5*d* to 21*d*, 4*f* to 12*f*, 5*g* to 6*g*, and 6*h*.

Table I gives the doublet intervals of the first few doublets of each series with references to the sources from which they are obtained. The negative sign indicates that the ^{2}F doublets are inverted. This effect is also found in some ^{2}F and ^{2}D doublets of the other alkali metals and has been generally ascribed to perturbations by excited states of the core electrons.[79–83] The principal series doublets obey closely the law $\Delta\nu \propto 1/n^{*3}$, where n^* is the effective principal quantum number.[10]

TABLE I. - DOUBLET INTERVALS IN THE SPECTRUM OF Cs I

n	4	5	6	7	8	9	10
$\Delta(n^2P)$cm.$^{-1}$	–	–	554·11[6]	180·478[7]	82·64[10]	44·66[10]	26·86[10]
$\Delta(n^2D)$cm.$^{-1}$	--	97·589[8]	42·88[6]	20·97[86]	11·69[86]	7·16[86]	4·68[86]
$\Delta(n^2F)$cm.$^{-1}$	−0·177[8]	−0·147[8]	−0·102[8]	−0·069[8]	−0·044[8]	−0·025[8]	−0·007[8]

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Beutler has found in absorption 115 lines of the so-called Cs I^b spectrum,[11] arising from excitation of an electron from an inner shell, in this case the $5p^6$ shell. He classified 54 of these as transitions belonging to the $5p^6\ 6s - 5p^5\ 6s\ ns$ and $5p^5\ 6s - 5p^5\ 6s\ nd$ series, having as limits the excited $5p^5\ 6s\ {}^3P$ and ${}^1P$ terms of Cs II. Beutler's terms are included in 'Atomic Energy Levels.'[86]

Forbidden lines of the $6s - nd$ series have long been known in both emission and absorption.[12-14,18,22] Measurements of their intensity are in agreement with the transition probabilities to be expected for quadrupole radiation.[14,15] This series was recently extended by the absorption measurements of Kratz and Mack[16] as far as $21d$, the doublets being resolved up to $16d$. The forbidden $p - p$ series has been found in emission.[17] The appearance of both the $s - d$ and $s - s$ series in absorption in external electric fields is referred to under the Stark effect.

The continuous emission (recombination) spectrum of cæsium has been investigated in several different sources.[17-23,27-29] A detailed study of the recombination process in a discharge tube has been made by Mohler and others with reference to the intensity distribution, the probability of recombination into different states, and the effects of electron concentration and velocity.[22,23,27-29] The continuous absorption (photo-ionization) spectrum has also been closely investigated.[24-26,30-35] The variation of atomic absorption coefficient with frequency has been deduced from both space charge[24,25,30] and direct absorption[26,31-33] measurements. In the presence of a foreign gas the absorption is found to fall as the gas pressure is increased.[31-34] Ditchburn *et al.* have compared the variation of atomic absorption coefficient with frequency in all the alkali-metal vapours:[35] in cæsium the characteristic minimum of the curve lies from 0·56 to 0·8 e.V. below the series limit. Quantum-mechanical calculations of continuous absorption coefficients as a function of frequency have been compared with the experimental results.[34,35,84,85]

The measurement of transition probabilities in atomic lines has been discussed fully by Mitchell and Zemansky,[64] and more recent work is referred to by Unsöld.[65] In the case of cæsium, the transition probabilities of some members of the principal[36] series and of the sharp and diffuse series[37,38] have been found from their absolute intensities in emission. Total absorption measurements[39,40] and the methods of magneto-rotation[41-43] and anomalous dispersion[44] have also been used to calculate transition probabilities for the first few members of the principal series. Measured intensities have been discussed with reference to thermodynamical equilibrium in the sharp and diffuse series.[45]

Considerable attention has been devoted to the doublet intensity ratio in the principal series. Early experiments gave conflicting results, with an indication that the ratio is near its theoretical value of 2:1 for the first two doublets, but rather greater for higher members.[36,40,43,46-50] Further experiments on the second doublet have given values mostly ranging between 3:1 and 4:1;[51-53,55-58] but the ratio appears to vary widely with experimental conditions and to depend, in particular, on whether the measurement be made in absorption or in emission.[51,52,55,56] Values between 4·6:1 and 10:1 have been found for the third member of the principal series[54,58-60] and yet higher values for higher members.[59] Fermi has suggested a theoretical explanation of the departure from the 2:1 rule.[61-63]

Little theoretical work has been done on the spectrum of cæsium. Although, as stated earlier (see page 2416), the spectra of this and the other alkali metals were much studied in connection with the development of the theory of atomic spectra, calculations of energy levels for atoms as heavy as cæsium have seldom been carried beyond the semi-empirical stage.[70,71] Before the advent of modern quantum mechanics, energy levels in cæsium were

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calculated from modifications of the Bohr theory[66,67] and by Fermi's statistical method.[68,69] Various empirical and semi-empirical formulæ have been applied to doublet separations.[72-75]

The application of quantum mechanics to the determination of atomic energy levels and eigenfunctions has been fully set out by Condon and Shortley.[76] Hartree in 1946 summarized the calculations carried out up to that date on the spectra of all light and a few heavy atoms for states of ionization up to the fourth.[77] For caesium, the only published values of wave functions appear to be self-consistent field functions without exchange for the ground state of Cs$^+$.[78]

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The Spectrum of Ionized Cæsium

Singly Ionized.

Lines of the Cs II spectrum have been identified in several forms of light source besides the spark, for example in certain combustion and collision processes[2,3] and in interrupted arcs,[7] as well as in the types of source useful in systematic investigation of the spectrum such as ordinary glow discharges[8,9,10] and electrodeless[6,11,14,15,17,18] and hollow-cathode[12,13] discharges. The conditions of excitation in sparks have been studied.[4,5,8]

Cs II in the ground state has the xenon-like electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ {}^1S_0$, with an ionization potential of about 25·1 v.[20] The wave-lengths of many lines were measured by early investigators and some of the lines classified by comparison with the rare gas spectra.[6,9-11] The results of these and subsequent measurements and classifications[12,13] were incorporated in the 1932 tables of "Atomic Energy States" by Bacher and Goudsmit.[1] Considerable extensions to the spectrum were made in the next few years,[14-16] and in 1941–2 Wheatley and Sawyer[17,18] measured

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850 lines and classified many new transitions. Their table of energy levels and observed transitions incorporates the earlier results,[18] and their term values are reproduced in the National Bureau of Standards "Atomic Energy Levels".[20] Since terms for which the excited electron is in an *nd* state fall very close to those in which it is an $(n+1)s$ state, it has not been possible to distinguish these two configurations for the higher *n*-values. The 79 term values listed arise from the $6p$, $7p$, $6s$, $7s$, $5d$, $6d$, and $(8s+7d)$ configurations of the excited electron built on both the $5p^5\ {}^2P_{3/2}$ ground term and the $5p^5\ {}^2P_{1/2}$ excited term of Cs III and in addition the $(9s+8d)$, $10s$, nf configurations on the ${}^2P_{3/2}$ term only.

Doubly Ionized.

The only measurement made on the iodine-like spectrum of Cs III is of nine pairs of lines from unknown upper levels to the $5s^2\ 5p^5\ {}^2P_{3/2,1/2}$ ground term doublet, giving a doublet separation of 13,884 cm.$^{-1}$[19,20] By extrapolation the ionization potential is estimated to be about 34·6 volts.[20,21]

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Zeeman, Stark and Pressure Effects

Zeeman Effect.

The Zeeman effect in the alkali-metal doublets is described in standard text-books on spectroscopy (see, e.g., page 2417). Rather fuller accounts have been given by Back and Landé.[1,2] As the historical resumés in these books indicate, the 'anomalous' Zeeman pattern of the resonance lines of the alkali metals played an important part in the development of spectroscopic theory.

The Landé *g*-factor for the ${}^2S_{1/2}$ ground state of caesium is 2, and for the ${}^2P_{1/2}$, ${}^2P_{3/2}$ levels it is 2/3 and 4/3 respectively. Thus, in terms of the classical Lorentz splitting $\Delta\nu_L$, the ${}^2S_{1/2}$–${}^2P_{1/2}$ line has two σ components at $\pm\frac{4}{3}\Delta\nu$ and two π components at $\pm\frac{2}{3}\Delta\nu_L$, while the ${}^2S_{1/2}$–${}^2P_{3/2}$ line has four σ components at $\pm\frac{2}{3}\Delta\nu_L$, $\pm\frac{5}{3}\Delta\nu_L$ and two π components at $\pm\frac{1}{3}\Delta\nu_L$. The Paschen–Back effect sets in with magnetic fields strong enough to break down the spin-orbit coupling; as this condition is approached, the components of the two resonance lines merge to form a Lorentz triplet with unshifted π component and σ

components at $\pm\Delta\nu_L$. The Zeeman effect in the alkali metals has been treated theoretically on the basis of Dirac's theory.[4]

The Zeeman effect in the ground state of caesium has received much attention in atomic-beam magnetic resonance experiments (**see also page 2424**), in the course of which extremely accurate measurements of the Zeeman splitting have been made.[5] The $g(6^2S_{1/2})$ value of caesium is found to differ from the $g(^2S_{1/2})$ values of the ground states of the three lightest alkali metals by $13:10^5$ and from that of rubidium by about $8:10^5$. Reasons for this discrepancy have been suggested.[6]

The magnetic double refraction of caesium vapour has been measured and compared with the calculated effect.[7] The appearance of 'forbidden' components in the Zeeman pattern of the resonance lines has been described[8,9,11] and calculations made of their intensity.[10,11] Pressure broadening of the Zeeman components has also been investigated.[12]

The simple Zeeman pattern in any field is symmetrical about the field-free line. However, at high fields and for the higher members of a series, the pattern as a whole may be asymmetrically shifted by the so-called quadratic Zeeman effect. Theoretically, the centre of gravity of the σ components should be shifted twice as far as that of the π components, the shift being proportional to H^2 and to $(n^*)^4$, where n^* is the effective quantum number.[15] Experimental results for the principal series of caesium are in reasonably good agreement with the theory.[14] The appearance of 'forbidden' components in the higher terms has been attributed to spin-orbit interaction.[13]

Stark Effect.

The Stark effect is rather briefly discussed in most text-books. A fuller account has been given by Minkowski.[3] The Stark pattern of a line is considerably more complicated than its Zeeman pattern. In the alkali metals the first-order effect is a quadratic one: an asymmetric splitting proportional to the square of the field strength, which, when unresolved, appears as a simultaneous broadening and shift of the line. The theory of the effect in the alkali metals has been discussed in several papers.[16-18]

Experimental investigations appear to have been confined to absorption measurements on the principal series.[19-22] These show the quadratic effect,[19-21] but in higher members of the series the linear effect appears.[22] The electric field also has the effect of bringing up lines of the forbidden $s - s$ and $s - d$ series, and its effect on the intensities and positions of these lines has been discussed.[21,22]

Pressure Effects.

General accounts of the effects of pressure on spectral lines may be found in text-books[23,24] and in the review articles written in 1936 by Margenau and Watson[25] and in 1957 by Ch'en and Takeo;[26] both the latter contain references to experimental work on alkali spectra, on which some of the most extensive research has been done, and accounts of the theories of pressure effects, including the Stark effect due to inter-atomic electric fields. More detailed theoretical papers have been published on both foreign gas broadening[27-30] and 'resonance' (self-pressure) broadening.[31,32]

Several measurements have been made of the broadening and shifts of the first three doublets of the caesium principal series in absorption in the presence of different foreign gases at pressures up to about 100 atm.[12,33-37] The direction of the shift depends on the line studied and the gas used;[33-36] the broadening is different for the two members of a doublet.[36] A number of measurements has also been made on higher members of the principal series.[37-40] The shift, which again depends in magnitude and direction on the foreign gas used, appears to increase steadily with the series number. The effect of the presence of a foreign gas upon the continuous absorption has been investi-

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gated and compared with the theoretical effect;[41,42] at a few cm. pressure the continuous absorption is reduced to about half.

The appearance of bands near the absorption lines of caesium has been attributed to the formation of loosely bound polarization molecules.[43-45]

The broadening of the resonance lines with increasing pressure of caesium vapour has been measured and compared with theoretical line contours.[46,47]

The quenching of caesium fluorescence by helium has been investigated.[48]

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Hyperfine Structure and Nuclear Moments

Before the development of magnetic resonance techniques, nuclear moments were determined primarily by optical investigation of the hyperfine structure (hereafter referred to as hfs). Kopfermann[1] has given a very full account of the theoretical background and of the methods of both optical and radiofrequency spectroscopy, and Ramsey[2] has summarized the application of these methods to the determination of nuclear moments, giving tables of results up to 1952 and many references. Nuclear effects in atomic spectra[35] and the role of nuclear moments in the shell model of the nucleus[37] have recently been reviewed.

The data for the caesium isotopes are summarized in Table II, in which references are given for the results published since 1952 and therefore not included by Ramsey.[2]

TABLE II. - NUCLEAR MOMENTS OF THE CAESIUM ISOTOPES

Isotope	I	μ (n.m.)	Q ($\times 10^{-24}$ cm.^{2})	$\Delta\nu(6^2S_{1/2})$ Mc/s	cm.$^{-1}$
^{127}Cs	½[24]				
^{129}Cs	½[24]				
^{130}Cs	1[24]				
^{131}Cs	5/2[22]	+3·48[22] ±0·04		13,200[22] ± 110	0·440
^{133}Cs	7/2	+2·57893[28] ±0·00003	−0·003[31,33] ±0·002	9,192·631830[20] ± 0·000010	0·3066
^{134}Cs	4[22,23]	+2·9900[28] ±0·0010		10,473·626[28] ± 0·015	0·3494
^{135}Cs	7/2	+2·7290[28] ±0·0010		9,724·023[28] ± 0·015	0·3244
^{137}Cs	7/2	+2·8219[28] ±0·0010		10,115·527[28] ± 0·015	0·3378

In this Table, I is the nuclear spin, μ the nuclear magnetic moment (in nuclear magnetons) and Q the nuclear electric quadrupole moment. The columns headed $\Delta\nu(6^2S_{1/2})$ refer to the splitting between the two hyperfine levels of the $6s$ $^2S_{1/2}$ ground state; this has been measured much more accurately by radiofrequency methods than is possible optically (as has the magnetic moment),[36] but for convenience the first few figures of the value have here been converted to cm.$^{-1}$

Hyperfine structure in the caesium spectrum was first examined in the second doublet of the principal series of the only naturally occurring isotope, ^{133}Cs.[3-9] The value for the spin of 7/2, obtained from intensity measurements,[5,6] was at first subject to considerable disagreement among different observers,[4,7,8] but was confirmed by the hfs of several terms in the Cs II spectrum.[10] The magnetic moment was calculated from the hyperfine splittings of the ground and higher states, in which there was fair agreement between the results of different experiments.[6,9] An average of the values found is given below.

State	$6^2S_{1/2}$	$6^2P_{1/2}$	$6^2P_{3/2}$	$7^2P_{1/2}$	$7^2P_{3/2}$	$8^2P_{1/2}$
$\Delta\nu$(cm.$^{-1}$)	0·306	0·038	0·018	0·012	0·007	0·007

The hfs of the Zeeman pattern was subsequently resolved[11,12] and the spin value confirmed from the number of components; their separation was in agreement with the theory. Work on the hfs of the alkali metals was reviewed in 1939,[13] and since then further work on the hfs of certain terms of Cs II has been used to find interval factors and establish J-values for these terms.[14]

In the recent absorption measurements of Kratz on the principal series,[38] the hfs of the ground term was resolved throughout, the value ranging from 0·29 to 0·34 cm.$^{-1}$

The most accurate measurements of nuclear moments and of the hfs and Zeeman levels of the ground state have been made by radiofrequency methods, mainly in atomic and molecular beams.[1,2,36] The atomic beam method of zero moments was early applied[15] to find the spin and hfs of ^{133}Cs. Later, Rabi's magnetic resonance technique was used in atomic beams to measure accurately the ground state hfs and Zeeman effect[18,19] and in molecular beams to measure directly the nuclear magnetic moment.[16,17] A microwave absorption method has also been used to measure the ground-state hfs;[39] and with the nuclear magnetic resonance technique a very accurate value has been found for the ratio of the magnetic moment of ^{133}Cs to that of the proton.[25–28]

An interesting application of atomic beam magnetic resonance measurements is the projected use of the caesium ground-state hyperfine splitting, 9192 Mc./sec., as a frequency standard. 'Atomic clocks' have been built in both England and the U.S.A.,[20,40–42] and that at the National Physical Laboratory is now stated[42] to be accurate to 2 parts in 10^{10}.

Magnetic resonance experiments on atomic beams of radioactive isotopes have given values for the spins of ^{127}Cs, ^{129}Cs, and ^{130}Cs,[24] and for the spins and ground-state hfs (and hence for the nuclear moments) of ^{135}Cs and ^{137}Cs;[21,28] ^{134}Cs;[22,23,28] and ^{131}Cs.[22] The results are given in Table II. In experiments on the isomer ^{134m}Cs the values obtained were $I = 8$, $\Delta\nu = 3675 \pm 0{\cdot}6$ Mc./sec., $\mu = +1{\cdot}1$ n.m.[43–46]

The variation of the ratio of hyperfine splitting to nuclear magnetic moment from one isotope to another, the so-called hfs anomaly, or Bohr–Weisskopf effect, is of interest in problems of nuclear structure, since it arises from the distribution of the magnetic moment over a finite nuclear volume.[29,30] The effect has been measured in caesium for the isotopes 133, 134, 135, 137.[28]

Recently Rabi *et al.* have succeeded in performing atomic beam magnetic resonance experiments with alkali-metal atoms in excited ^{2}P states, and from transitions between hyperfine levels of the $6^2P_{3/2}$ state of ^{133}Cs they have found the magnetic hfs constant of this state and the nuclear electric quadrupole moment ($-0{\cdot}003 \times 10^{-24}$ cm.^{2}).[31] In addition, the hfs of the $7^2P_{3/2}$ state has been investigated by the very recent technique of magnetic double resonance, whereby radiofrequency transitions between hyperfine levels are detected optically.[32,33] The value of Q found is in excellent agreement with the atomic beam value. Calculations of intensities in these experiments have been compared with experimental results.[34]

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X-Ray Spectrum

Early work on the *X*-ray spectrum of caesium was principally concerned with measurements of the wave-lengths and intensities of the *K*- and *L*-series lines and absorption edges.[1-4] Work on *N*- and *O*-series lines has also been reported.[5] A table of atomic energy levels has recently been compiled from *X*-ray frequencies for caesium and other light and medium elements.[6]

Later work has included an examination of the structure of the *K* absorption edge in crystals[7] and of the *X*-rays emitted by ^{131}Cs in the course of decay.[8]

Some general accounts and reviews refer to the *X*-ray spectrum of caesium, with particular emphasis on the importance of *X*-ray spectroscopy in solid-state physics.[9-11]

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THE MOLECULAR SPECTRA OF CÆSIUM AND CERTAIN OF ITS COMPOUNDS

By R. F. BARROW

The Cs_2 Molecule

A large number of bands have been observed in the spectrum of cæsium vapour and attributed to the Cs_2 molecule. They appear readily in absorption,[1,2] and have been observed in fluorescence[1,3,8] and in excitation by active nitrogen.[4] Although a number of attempts has been made,[5-7] the fact that the values of ω are so small makes analysis difficult, and only that of the system B-X seems well established.[8] At least four other excited states of this molecule have been recognized[8-10] (see Table III), but one system originally ascribed to Cs_2 was later shown to arise from RbCs.[10,11]

TABLE III. SPECTROSCOPIC CONSTANTS FOR Cs_2

State	ν_e	ω_e	$x_e\omega_e$	D_0, kg.-cal.
E	~20500	~31	-	-
D	(16175·80)	(27·34)	(0·0733)	-
C	(16066·03)	(29·38)	(0·0796)	-
$B(^1\Pi_u)$	13043·87	34·230$^{(1)}$	0·077986	6·7±1·0
$A(^1\Sigma_u^+)$	~10000	- -	-	-
$X^1\Sigma_g^+$	0	41·990$^{(2)}$	0·080051	10·4±1·0

Notes: (1) $-1{\cdot}64266 \times 10^{-4} (\nu + \frac{1}{2})^3$
(2) $-1{\cdot}88149 \times 10^{-4} (\nu + \frac{1}{2})^3$

Diffuse bands arising from loosely-bound polarization molecules of Cs-Cs[12-15] and of Cs with various foreign gases[16-18] have also been observed.

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Cæsium Hydride

The system $A^1\Sigma^+ - X^1\Sigma^+$ has been observed in absorption in the region 4550 to 6250A. Constants are as follows:-

State	T_e	ω_e	$x_e\omega_e$	$y_e\omega_e$	D_0, kg.-cal.
$A^1\Sigma^+$	18405·2	204·0	-5·70	-0·350	-
$X^1\Sigma^+$	0	890·7	12·6	-	44

State	B_e	α_e	r_e, A.
$A^1\Sigma^+$	1·126	-0·0185	3·869
$X^1\Sigma^+$	2·709	0·057	2·494

The assignment of vibrational quantum numbers in state A may need revision. A comparative account of the spectra of the alkali metal hydrides has been given[2] (see also page 280).

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Cæsium Halides

Accurate values for the molecular constants of the gaseous cæsium halides have been obtained from the study of their absorption spectra in the microwave region.[1] The spectrum of cæsium chloride has been examined in absorption in the vibration-rotation region of the infra-red;[2] this work leads to a value for the vibration frequency of the gaseous molecule.

Studies of the electronic spectra of these molecules have been reported as follows: cæsium fluoride,[6] chloride,[5,6] bromide[3,4,6] and iodide.[4-6]

The molecular-beam electrical resonance method has been applied to investigations of the molecular properties of cæsium fluoride[7-10] and cæsium chloride.[11] The molecular-beam magnetic resonance spectrum of cæsium fluoride has also been studied.[15]

Values of the molecular constants of the cæsium halides are collected in Table IV together with the thermochemical information required for the determination of their energies of dissociation (see also page 283).

TABLE IV. SPECTROSCOPIC CONSTANTS FOR THE GASEOUS CAESIUM HALIDES

Molecule	B_e	α_e	r_e, A.	ω_e, cm.$^{-1}$	μ, D.
CsF	5527·34	33·13	2·3453	(330)(4)	7·87
CsCl	2161·21(2)	10·085(2)	2·9062	209	10·40
CsBr	1081·34(3)	3·718(3)	3·0720	[139]	-
CsI	708·36	2·044	3·3150	[101]	12·1

Notes: (1) The values of B_e, α_e and r_e are taken from reference 1. The values of B_e and α_e are in Mc./sec.

(2) Constants for $Cs^{35}Cl$.

(3) Constants for $Cs^{79}Br$.

(4) ω_e (CsF) = 385cm.$^{-1}$ from ultra-violet spectrum,[6] 270±30cm.$^{-1}$ from molecular-beam electrical resonance.[9] Other values of ω_e are from reference 2: values in square brackets are estimated values.

continued on following page.

TABLE V (continued)

Dissociation Energies, D_{298}, kg.-cal.mole^{-1}				
	CsF	CsCl	CsBr	CsI
$-Q_f$(MX)	126·9[a]	103·5[a]	94·3[a]	80·5[a]
$-\Delta_s H$(MX)	-49·1[b]	-49·6[d]	-48·4[d]	-49·3[d]
$\Delta_s H$(M)	18·83[c]	18·83[c]	18·83[c]	18·83[c]
Q_f(X)	18·86[d]	29·01[a]	26·71[a]	25·48[a]
D_{298}	115·5	101·7	91·4	75·5

a reference 12
b reference 13
c reference 14
d recalculated from reference 16

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COMPOUNDS OF CÆSIUM: SOLID STATE

Cæsium Hydride

The ultra-violet absorption of thin layers of cæsium hydride deposited on quartz has been examined.[1] Maxima occur at 2970 and 2180A.

Reference

1 Rauch, W., *Z. Phys.*, 1939,**111**,650-6. (*33*,6155)

Cæsium Oxide, Cs_2O

Maxima[1] in the ultra-violet absorption spectra of thin films of cæsium oxide deposited on quartz lie at 3760, 2700, 2570 and 2070A.

Reference

1 Rauch, W., *Z. Phys.*, 1940,**116**,652-6. (*35*,4682)

Cæsium Halides

In order to avoid repetition, certain properties of the crystalline alkali metal halides are only discussed in detail under one appropriate alkali metal, as follows: ultraviolet absorption spectra, page 285; Raman spectra, page 1380; colour centres, page 2012; luminescence: phosphors, page 2018.

The absorption spectra of the crystals have been studied in both the infra-red and ultra-violet regions. In the infra-red, maxima have been observed[1] as follows:-

CsCl: 102·0μ. CsBr: 134·0μ.

In the ultra-violet region, the maxima[2-4] lie at the following wave-lengths:-

CsF: 1360 1180 1100 A.
CsCl: 1620 1450 1370 1190 A.
CsBr: 1870 1730 1600 1460 1200 A.
CsI: 2180 2060 1850 1770 1630 1470 1300 A.

(see also page 285).

Theoretical treatments of the Raman effect in cæsium halide crystals have been discussed.[5,6]

Cæsium bromide and cæsium iodide have applications as materials for prisms in spectrographs for the long wave-length infra-red region.[7-9] The bromide has been used[8] as far as 38μ, and the iodide[9] up to 54μ.

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SECTION XCVI

THE ANALYTICAL DETERMINATION OF CÆSIUM

By H. V. THOMPSON

DETECTION

A number of qualitative reactions common to both rubidium and cæsium have been given in the corresponding section under Rubidium (see **page** 2275).

A very dilute solution of potassium ferrocyanide and either calcium or magnesium chloride gives a precipitate with a solution of a cæsium or rubidium salt and it is claimed that in the absence of the latter element this test is the most sensitive known for cæsium.[1,2] The formation of orange-red hexagons when a crystal of potassium iodobismuthite is added to a drop of the test solution indicates the presence of cæsium or of comparatively large amounts of rubidium.[3,4] The test is considered to be characteristic for cæsium provided that not more than a 50-fold excess of rubidium is present. A sensitive test for cæsium is the formation of a complex chloride with zinc and gold having a well defined micro-crystalline structure.[5] Provided rubidium is absent, 12-phosphomolybdic acid will detect as little as one part of cæsium in 500,000 of water.[6] A microchemical test for cæsium has been based on the formation with a nickel salt of a crystalline double phosphate, $NiCsPO_4$, but an analogous compound is given by rubidium in concentrations of 0·1% and over.[7]

Under appropriate conditions the following tests are said to be specific for cæsium by the formation of:- (i) a yellow-orange precipitate with potassium ferricyanide and lead acetate,[8] (ii) a faint yellow precipitate with a solution of silver nitrate in sodium iodide in presence of alcohol[9] and (iii) a dark red microcrystalline precipitate with cadmium iodide and hydrochloroplatinic acid.[10]

DETERMINATION BY CHEMICAL METHODS

Gravimetric Methods.

Methods for the separation of cæsium and rubidium and of rubidium from cæsium have been outlined under Rubidium (see page 2276).

In the silicotungstate procedure,[11] the silicotungstic acid is removed as its mercurous salt from a faintly acid solution of the precipitated cæsium complex in nitric acid, and the cæsium is determined in the concentrated filtrate as chloroplatinate after oxidizing the excess of mercurous nitrate to the mercuric state. When cæsium has been separated from rubidium as cæsium antimony chloride,[12-14] the antimony is eliminated from the solution of the precipitate and the cæsium is subsequently determined as perchlorate.

Other methods proposed for the determination of cæsium in the presence of rubidium are precipitation as cæsium stannic bromide,[15] Cs_2SnBr_6, or as cæsium sodium lanthanum nitrite,[16] $Cs_2NaLa(NO_2)_6$, provided in both instances that rubidium is not present in very large excess; in the second method the determination can be completed gravimetrically or volumetrically by titrating the nitrite with ceric sulphate. In the presence of the other alkali metals, it is claimed that 5 mg. of cæsium and upwards can be determined with a satisfactory degree of accuracy by precipitation as its double iodide, $Cs_3Bi_2I_9$, with a solution of bismuth iodide in hydriodic acid.[17,18] For the determination of cæsium as its tetraphenyl boron complex see pages 2027, 2276.

By an extension of the volumetric method for the determination of rubidium (see page 2276), cæsium can be subsequently determined.[18a]

DETERMINATION BY PHYSICAL METHODS

Reference has already been made to the value of spectrography for the determination of cæsium and rubidium especially when present in amounts below the effective range of gravimetric methods (see page) and various papers have been published dealing specifically with the spectrographic determination of cæsium.[19-22] A limited amount of work has been done on colorimetric methods for determining cæsium.[23] In one process the cæsium is precipitated as silicomolybdate; the molybdenum in the precipitate is reduced by stannous chloride to molybdenum blue and the colour compared with similarly prepared standards.[24]

Cæsium in sea water has been determined by radioactivation.[25a] Partition chromatography on paper has been applied to the complete separation of very small quantities of the chlorides of potassium, rubidium and cæsium.[25] Methods for the concentration and determination of cæsium in living organisms have been reviewed by Bertrand and Bertrand[26] and references to other reviews are given under Rubidium (see page 2276).

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SECTION XCVII

BIOLOGICAL PROPERTIES OF CAESIUM

By F. CALL

Although cæsium appears to be one of the most toxic of the alkali metals, this toxicity is not of a high order and the element is taken up by many plants and micro-organisms, often with a stimulating effect. The difference in the ionic radii makes cæsium a relatively poor replacement for potassium in living cells. The occurrence of ^{137}Cs among the fission products resulting from atomic explosions has stimulated investigation into the uptake of this isotope by plants and its accumulation in animals feeding on the plants.

Micro-organisms

Cæsium stimulates the growth of *Aspergillus niger*[1] and the fermentation of yeast[2] while the luminescence of phosphorescent bacteria is stimulated by low concentrations.[3] The glycolysis of resting cells of *Lactobacillus arabinosus* is completely inhibited by cæsium ions if insufficient potassium is present.[4] Many species of bacteria rapidly adapt themselves to toxic concentrations of cæsium salts.[5] Cæsium is the most effective of the alkali metals in producing morphological changes in *Serratia marcescens*[6] and other species of bacteria[7] and algæ.[8] Negligible amounts of ^{134}Cs were removed from laundry wastes during their biological oxidation by the micro-organisms present in the slimes and sludges.[9,10]

Soil and Plants

Spectrographic analysis has shown cæsium to be present in many soils.[11] The uptake of cæsium by plants from soils is inversely proportional to the available soil potassium[12] and also depends on the particular clay mineral predominant in the soil, being greater from soils containing illite and kaolinite than from soils containing montmorillonite.[13,14] Cæsium is removed from solution in water by percolation through soils.[15]

Cæsium is accumulated from sea water by many marine algæ, often being enriched several thousand-fold.[16] Potato plants take up only about 20% of the available cæsium from nutrient solutions. At the higher concentrations, which are toxic, the roots tended to accumulate cæsium in preference to potassium.[17] The rate of absorption of cæsium from solution by rice increases with concentration of the ion,[18] in contradistinction to the absorption of rubidium the rate of which bears no relation to the aqueous concentration. There is a correlation between the amounts of potassium, rubidium and cæsium absorbed by a number of different plants from nutrient solutions.[19] Kinetic studies of the uptake of alkali metals by barley roots indicates competitive interference between potassium, rubidium and cæsium suggesting that these three ions are fixed at the same binding site in the roots whereas sodium and lithium appear to be fixed at quite different sites.[20] The absorption of cæsium by carrot discs and barley roots is inhibited by the metabolic inhibitors, dinitrophenol and azide ion, thus providing further evidence that initial fixation of the alkali metal occurs through some metabolic mechanism.[21] The absorption of cæsium by the secondary phloem of carrots proceeds by two different mechanisms. If the cells are dividing rapidly, cæsium is taken up on sites provided by the synthesis of new protein, the absorption being associated with a cyanide-insensitive respiration. If, however, the cells are not actively dividing cæsium accumulates in the vacuole by a mechanism which is cyanide-sensitive. There is some evidence that cæsium passes up the roots of the narcissus in waves.[22] The translocation of cæsium ions after application to the leaves of bean plants is independent of that of phosphate applied to the same site and is inhibited by low temperatures, the optimum temperature being 30°C.[23] Cæsium absorbed from nutrient solution through the roots of maize becomes uniformly distributed throughout the plant.[24,25] Studies of the plasmolysis of protoplasts show that the epidermal cells of *Oenathera franciscana* take up water by a non-osmotic mechanism when immersed in solutions of caesium nitrate.[26]

Cæsium salts at a concentration of 0.01% have a stimulating action on the germination of barley;[27] although wheat germinates in 0.006 N-cæsium solution, it dies in about 10 days.[28] Cæsium chloride at all concentrations tested decreased the rate of elongation of radish seedlings, an effect which was not due to the increased osmotic pressure of the solution.[29] The toxicity of cæsium salts as measured by the growth rate of the roots of *Lepidium sativum* could be reduced by the addition of an alkaline earth salt.[30] Rubidium-resistant mutants of *Ankistrodesmus braunii*, produced by long culture in rubidium solutions, were also resistant to the toxic effects of cæsium salts.[31] Cæsium salts produce cytological changes, mainly colchicine mitosis, in root meristems of *Allium cepa*,[32] but had only low activity in causing chromosome abnormalities in pea or beet seedlings.[33]

Animals

A higher content of cæsium has been determined spectroscopically in the retinas of ox, sheep and pig than in any other tissue examined.[34] After intravenous injection into dogs cæsium disappears rapidly from the blood plasma but is stored in the body, 17–39 days being required for the excretion of half the cæsium. After seven weeks 8–37% still remains in the body, 50–55% having been excreted via the urine and 8–14% via the fæces.[35] A similar retention has been observed in mice[36] and in rats, cattle, sheep, swine and chickens.[37] The highest concentration is found in muscle and the lowest in bone and plasma.[37,38] Such retention of radioactive cæsium would render the animal dangerous as a source of food. Cæsium has been stated not to penetrate into human erythrocytes[39] but in other experiments there was about 20% exchange between the erythrocytes and plasma.[40] Cæsium does not compete with either potassium or sodium for entry into the cells.[41] Cæsium can, however, partially replace potassium in the active salt and water uptake of frog skin.[2] Cæsium is taken up by frog muscle which has contracted during the perfusion but not by resting muscle. If taken up, the cæsium is not removed by perfusing the muscle with a potassium salt solution.[43] Higher concentrations of cæsium accumulate in tumour tissue than in normal tissues[44] although earlier work appeared to disprove this.[45]

Cæsium is the least toxic of the alkali metals to *Arbacia* eggs[46] and the toxicity to mammals is very low, though greater than that of rubidium.[47,48] The general physiological and pharmacological properties resemble those of the quaternary ammonium bases.[49] The action on isolated organs, such as the frog heart,[50-53] the pig uterus,[54] nerves[55,56] or the *Aphysia* crop[57] is slight and resembles that of potassium, but cæsium is not so effective a substitute for potassium as is rubidium.[58] Cæsium is less effective than potassium in maintaining the motility of ram and bull spermatozoa.[59] The effect of cæsium salts on respiration depends on the tissue and on the species.[60] Thus, the

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aerobic glycolysis of rat brain tissue is decreased by cæsium salts[61] while the respiration of rat liver mitochondria is increased.[62]

Cæsium chloride is as effective as potassium chloride in stabilising a plant carbonic anhydrase[63] but cæsium ions inhibit glycolysis by a cell-free extract of *Lactobacillus arabinosus*[64] although an apyrase from the same species is stimulated.[65]

Injections with cæsium salts appear to give some protection to animals against infection with bacteria of the paratyphoid group and with tubercle bacteria. This therapeutic action depends on the diet and is enhanced during starvation.[66-69] The use of radioactive cæsium in biology has been reviewed and the element has been proposed as an agent for sterilising food and drugs.[70]

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CHAPTER 6

RADIOCHEMISTRY OF THE ALKALI METALS

SECTION XCVIII

TABLE OF ALKALI METAL ISOTOPES

The following table of data on the radioactive and stable isotopes of the alkali metals has been prepared principally from the 'Table of Isotopes' by J. M. Hollander, I. Perlman and G. T. Seaborg dated December, 1952,[1] from 'Table of Isotopes' by D. Strominger, J. M. Hollander and G. T. Seaborg, 1958[2] and from "Nuclear Data Sheets" 1960,[3] with the kind permission of the authors.

This introduction, based on that of the original Table, has been amplified where necessary by Mr. J. L. Putman to render it more readily intelligible to readers whose interests are primarily chemical, and the selection of data for inclusion in these extracts from the Table has been made by Dr. R. A. Allen.

A description of the entries in various columns is given below, followed by a table listing some frequently used abbreviations.

ISOTOPE

The first and last columns list the atomic numbers, chemical symbols and mass numbers of the nuclear species. Separate entries have been made for each nuclear state whose half-life has been experimentally determined. Metastable excited states are denoted by the superscript 'm' following the mass number.

CLASS AND IDENTIFICATION

The degree of certainty of each isotopic assignment is indicated by a letter, according to the following code:-

A. Element and mass number certain.
B. Element certain and mass number probable
D. Element certain but mass number not well established
E. Element probable and mass number not well established or unknown (mass number not listed means that it is unknown).

Data which have been shown to be in error have in general been eliminated from the Table.

The means by which the mass assignments were made are next tabulated. In general, several references are given here in italics, the first of which denotes the probable discoverer of the isotope. Following this, references are given to the paper or papers which contributed most significantly towards giving the isotope its best or present rating. Some indication of the experimental methods used in making the various assignments may be had from the following symbolism:-

chem	Chemical separations, establishing uniquely the chemical identity (atomic number) of the isotope
genet	Proven genetic relationships (by chemical or other means) with other isotopes whose mass assignments are presumably known

excit	Loosely refers to energetic considerations which have aided in making the mass assignment. Some of these might be:- (1) Excitation or yield experiments to establish the nuclear reaction which produces the isotope (2) Bombardments with low energy particles, in which possible products are few (3) Mass calculations, or other estimates or measurements of Q values (4) In a few cases, use of fission yield data in making assignments
cross bomb	Studies of yields of the isotope in several different types of bombardments, in which the target elements as well as the projectiles have been varied
n-capt	Cases where bombardments with slow neutrons (n-γ reactions) have provided key evidence in the mass assignments
sep isotopes	The use of target elements enriched or depleted in a certain isotope
mass spect	Identification of the mass number by means of a mass spectrograph
decay charac	Identification of expected or predicted decay characteristics

PERCENTAGE ABUNDANCE

The relative isotopic abundances for the elements are given in accordance with the 'best values' listed in the report by K. T. Bainbridge and A. O. Nier[4] and the Nuclear Data Sheets. For some of the light elements reference is made also to papers which discuss source variations in isotopic abundance.

TYPE OF DECAY

The observed modes of decay have been listed for all radioactive nuclei. In cases of branched decay between two or more modes, the branching ratios are listed wherever they are known. Symbols used are:-

β^-	Negative beta particle (negatron) emission
β^+	Positive beta particle (positron) emission
α	Alpha particle emission
EC	Orbital electron capture. It may be assumed that *X*-rays have been observed or actually identified in virtually all cases of orbital electron capture listed. If the ratio of L electron capture to K electron capture has been determined, it is given here as L/K
IT	Isomeric transition (transition from upper to lower isomeric state of same nucleus)

When experimenters have searched for and failed to find a particular mode of decay, this is indicated, for example, as 'no β^+'. Experimental upper limits are frequently given, but no theoretically predicted limits have been quoted.

Among the heavy alpha-emitting isotopes, calculations by means of closed radioactive decay cycles have shown that many of these isotopes are thermodynamically stable against β^-, β^+ or EC decay. This has been indicated by the term 'β-stable', followed by an abbreviation for the principle of conservation of energy, which is used in the calculations.

HALF-LIFE

Half-life values are listed without qualification where the determination has been a direct measurement of decay rate. In other cases, the experimental methods have been described with the aid of the following symbols:-

sp act	Determination by weighing a long lived isotope of known purity
delay coinc	Measurement of the time interval between two successive nuclear events (such as β^- and γ emission) thus establishing the lifetime of the state responsible for the second event. By this method, half-lives between 10^{-3} s and 10^{-10} s have been determined
yield	Estimation of half-life from the amount of activity resulting from a nuclear reaction whose cross section (or yield) is known or estimated

An attempt has been made to list the best value or values first. However, in a few cases where many values of comparable precision have been reported and no choice seemed obvious, an average value for the half-life has been listed; this is explicitly stated, and references are given to all the papers whose values contributed to that average.

PARTICLE ENERGIES

The particle energies are followed by other relevant information pertaining to the decay scheme and by a description of the experimental methods used in obtaining the data. In cases of complex alpha structure or several partial beta spectra, the relative abundances of the various groups within that mode of decay are given in parentheses.

Beta particle energies correspond to the upper limits of the spectra.

Alpha particle energies have been quoted only where the investigator has actually measured them.

Conversion electron energies are listed only when it is not known in which shell internal conversion takes place or when no attempt was made by the experimenter to relate the electrons with observed or unobserved gamma rays; in all other cases, entries are made in the column for gamma transitions.

Experimental methods are described as follows:-

abs	*Absorption* of the radiation. The absorption of β^- and β^+ particles in increasing thicknesses of material is at first nearly exponential, but a maximum range is eventually reached. Both the initial absorption and the maximum range are measures of the original energy of the particles
coinc abs	β- and *γ-counters with absorbers* can be *coupled to a coincidence equipment,* which registers only when a count is obtained simultaneously in both counters. This method is sometimes used for the selection of particles or gamma-rays in complex breakdown schemes
spect	In a *beta-spectrometer,* the energy of the radiations is found from their deflection in a magnetic field
coinc spect	Denotes coincidence methods (see coinc abs) used in conjunction with a beta-spectrometer
scint spect	In the scintillation counter, radiations falling on a crystal, or other phosphor, produce scintillations of light which are converted to electrical impulses with a photomultiplier. Using certain phosphors, the amplitude of the impulses is proportional to the energy given up by the radiations. The arrangement can therefore

	be used as a *scintillation spectrometer* to determine energies of the radiations
cl ch	By the use of a Wilson cloud chamber the tracks of particles are made visible when vapour is condensed on the charged ions they leave behind. The cloud chamber is used with magnetic fields to determine the deflection and hence the energy of β^- and β^+ particles
ion ch	The ionization per cm. of path, as well as the total ionization, produced by a beta-particle depends on its energy. In the pulse *ion chamber* and in the *proportional counter*, electrical pulses are produced whose amplitude is proportional to the ionization in the chamber. These can be used to deduce the energy of the radiations.

GAMMA TRANSITIONS

Gamma transitions are described by the following information, in so far as reliable data permit:-

Energy of the gamma quantum. When internal conversion electrons form the basis for the energy determination, the energy listed in this column is always that of the corresponding gamma ray transition.

Abundance of gamma rays. This may be given as the number of unconverted gamma rays emitted per 100 disintegrations. Where an absolute abundance has not been determined, often the relative unconverted gamma ray abundances have been measured. These are tabulated, for examole as $\gamma_1/\gamma_2/\gamma_3 \approx 2/1/5$.

Internal conversion coefficients. These are given for each gamma transition as the ratio of the number of conversion electrons emitted to the number of unconverted gamma quanta emitted, and are expressed as e/γ. Where conversion coefficients for individual electron shells have been determined, they are denoted as $e_K/\gamma, e_L/\gamma$ etc.

Conversion coefficient ratios. Where the ratios of internal conversion coefficients in several electron shells have been measured, they are listed as K/L, L/M, K/L+M, K/L/M, $L_I/L_{II}/L_{III}$, etc.

When an author states that gamma radiation is present, but reports no energy determination, this is indicated by the symbol 'γ'. Conversely, when attempts to find gamma radiation have failed, this has been indicated by 'no γ'.

X-Rays have been mentioned only when they are the prominent radiation observed in measuring an activity, or when the observation and identification of *X*-rays has been crucial in the characterization of an isotope.

The symbols used to describe the methods employed for the determination of gamma ray energies or for the elucidation of decay schemes are as follows:-

abs	*Absorption* of the radiations. The number of gamma-ray quanta decreases exponentially with the thickness of the absorber, and the rate of decrease is a measure of their energy.
abs sec	*Absorption* of the *secondary electrons* produced by the photo-electric effect of γ-rays on matter. The energy of such photo-electrons is equal to that of the original γ-rays minus the ionization energy needed to eject the photo-electrons from atoms of the absorber.
abs conv	*Absorption of internal conversion electrons*
coinc abs	Coincidence studies using absorption techniques (see PARTICLE ENERGIES)
spect	Use of the magnetic beta-spectrometer (see PARTICLE ENERGIES) to measure the energy of *secondary electrons* produced by gamma-rays in matter

spect conv	Use of the beta-spectrometer (see PARTICLE ENERGIES) to measure the energy of *internal conversion electrons*
coinc spect	Use of the *beta-spectrometer* in connexion with other counters in a coincidence arrangement (see PARTICLE ENERGIES, coinc abs). Coincidences with other gamma-rays, with conversion electrons from other gamma-rays, with beta-particles etc. are used to identify the particular gamma-ray being measured and to determine its relation to the decay scheme of the radioisotope.
scint spect	(See PARTICLE ENERGIES). The energy of the gamma-rays is generally deduced from the pulses produced when gamma-rays are completely absorbed in the phosphor; *i.e.* from the energy of photo-electrons produced in the phosphor. It can also be deduced from the maximum energy of recoil electrons produced by the Compton recoil process in the phosphor
cryst spect	Estimation of wave-length and therefore energy from the *diffraction* of gamma-rays in a crystal. This is a standard method by which the wave-lengths of *X*-rays are determined in terms of the spacing between planes in the crystal structure. It is generally applied only to low energy gamma-rays, whose wave-lengths are not too short compared with the spacing of crystal planes

DISINTEGRATION ENERGY AND SCHEME

The disintegration energy (Q) of a nuclear decay process is defined as the mass difference of the initial and final atoms, transformed into units of energy (1 atomic mass unit = 931 MeV.). It is equal to the sum of the kinetic energies of the particles emitted, plus the energies of any gamma-rays which may follow them, plus the energy of recoil of the nucleus. Note that when positrons are emitted the energy (1·02 MeV.) of the annihilation radiations must be included. Where Q values have been estimated or calculated by the authors of this compilation, the special reference 'HPS' is used; otherwise, reference is made to the paper from which the quoted value is taken. In most instances Q values have been obtained from decay data; where this is not the case, the method is indicated.

Energy level diagrams have been drawn in many cases; these are not necessarily complete representations of the data, but sometimes include only those features which are reasonably well established and unambiguous. β^- particles are represented by lines sloping downwards from left to right. β^+ particles and electron capture processes are shown as lines sloping downwards from right to left. Gamma-rays are shown as vertical lines. Thus, vertical displacement represents loss of energy, and horizontal displacement represents change of atomic number. Where alternative modes of decay exist, all are shown, and the percentage of disintegrations proceeding by each mode is indicated. Heights of the various energy levels above the ground state are indicated at the side of the drawing. Similarly, the total angular momentum (spin) and parity of the states have been included in some cases, where these quantum numbers could be inferred with some confidence from determinations of conversion coefficients, K/L ratios, ft values, etc. We have relied heavily on the interpretation of decay data by Goldhaber and Hill.[5]

For β^-, β^+, α, or EC decay, the percentage figures given in the decay drawings total 100% for *each* mode of decay, thus expressing only the relative abundances of various groups within that mode of decay. (Branching ratios between the several modes of decay are found in the 'Type of Decay' column). In the case of gamma radiation, however, the percentages given refer to the fraction of the total disintegrations of that isotope which give rise to the gamma ray and its conversion electron. This has been done because of the difficulty of assigning a gamma ray to a particular mode of decay.

Measured values for the mechanical or spin moment, I, of stable or long lived isotopes have also been given in this column. Except as supplemented by more recent data, the values given here are taken from the compilation by Mack.[6]

METHOD OF PRODUCTION AND GENETIC RELATIONSHIPS

The last column of the Table gives the nuclear features (target element, projectile and outgoing particle, in order) by which the radioactive isotopes are formed. The corresponding references are listed: (p-proton, n-neutron, α-alpha particle, d-deuteron, t-triton, γ-gamma ray or X-ray, e-electron, π-pi meson, C-carbon ion). In cases in which the target material is not the naturally occurring element, but one enriched or depleted in a particular isotope, the isotope responsible for the reaction is indicated. No means for identifying the source or energy of the projectile are given.

In nuclear reactions with high energy projectiles, multiple particle ejection is common. Rather than attempting to state definitely the path by which the product nucleus was reached, these spallation reactions are briefly represented by the abbreviation 'spall', followed by the symbol of the target element. High energy fission reactions are similarly represented by the words 'spall-fission', and thermal or low energy neutron fission simply by 'fission'.

The criterion for listing genetic relationships has been with few exceptions that these relationships be demonstrated experimentally; for example, by chemical 'milking' of daughter activities, analysis of growth decay curves, or, in the case of short lived isomers, by delayed coincidence experiments. The listing of these parent-daughter relationships gives some warning to the reader as to what he may expect in the way of radiation from a given isotope, since a sufficiently short lived daughter's radiation will usually be observed with that of the parent.

A few further abbreviations are listed below:-

[ ]	Properties listed in brackets have not been observed directly, but have been inferred from other experimental data.
est calc	Estimated or calculated from theoretical or empirical considerations
lim	Experimental upper limit
emuls	Photographic emulsion

References

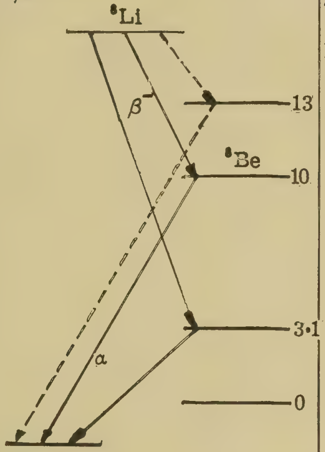
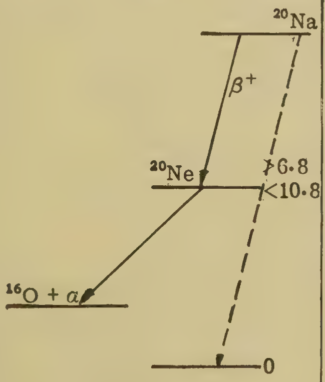
1 Hollander, J. M., Perlman, I. & Seaborg, G. T., *Document No. UCRL*, 1928, *Atomic Energy Commission, Rev. Mod. Phys.*, 1953,25,469-651. (*47*,8429)
2 Strominger, D., Hollander, J. M. & Seaborg, G. T., *Rev. Mod. Phys.*, 1958,30, 585—904.
3 Nuclear Data Sheets, National Academy of Sciences, National Research Council, Washington, Up to 1960 issues.
4 Bainbridge, K. T. & Nier, A. O., *Natl. Res. Council Nuclear Energy Series, Preliminary Report No. 9*, Dec. 1950.
5 Goldhaber, M. & Hill, R. D., *Rev. Mod. Phys.*, 1952,24, 179. (*47*, 2046)
6 Mack, J. E., *Rev. Mod. Phys.*, 1950,22,64. (*44*, 5205)

TABLE OF
ALKALI METAL ISOTOPES

TABLE OF ALKALI METAL ISOTOPES

Isotope	Class and identification	Percent abundance	Type of decay	Half-life	Radiation energy, MeV. Particles
$^{6}_{3}$Li		7·42[1]			
^{7m}Li	A excit[3]		IT[3]	5·2 × 10^{-14} s Doppler[3] broadening	
^{7}Li		92·58[1]			
^{8}Li	A excit;[4,5] n-capt, sep isotopes, genet[6]		β^-, 2α[5]	0·825 s;[7] 0·88 s;[8,9,10] 0·85 s;[11] 0·89 s[6] 0·841[361] 0·83[362]	β^-: 13 (~90%), ~6 (~5%), ~3 (~5%) spect;[12] <13 (~ 2%) β-γ coinc abs;[13] 12·0 cl ch;[8] abs;[9] two α's: total energy 3·2, 7–9 cl ch[14]
^{9}Li	B excit, cross bomb[25]		β^-, n[25,26]	0·168 s;[25] 0·170 s;[26] 0·19 s[11] 0·15[363]	
$^{20}_{11}$Na	A excit[27]		β^+, α[27,28]	0·385 s;[29] 0·23 s[28] 0·25[364]	3·5<β^+<7·3 est[28]

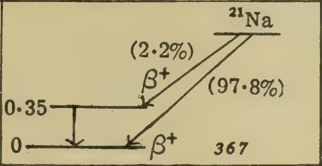
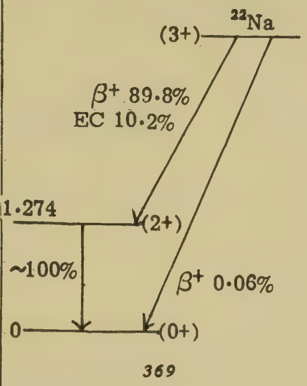
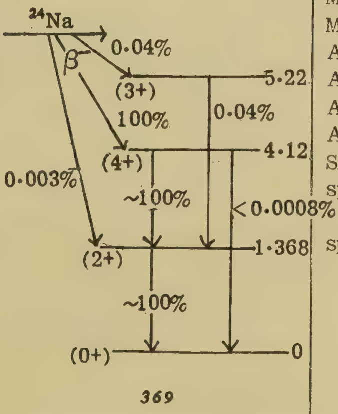
TABLE OF ALKALI METAL ISOTOPES

Radiation energy, MeV. γ-Transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
	^{6}Li, I = 1[2]		$^6_3$Li
~0·48 spect[3]		B-n-α[3]	^{7m}Li
	^{7}Li, I = $^3/_2$[2]		^{7}Li
no γ;[8,15] γ (very weak) β-γ coinc[13]	Q_{β^-} 15·99[16]  12	Li-n-γ;[17,18,6] ^{7}Li-n-γ;[6] Li-d-p;[4,19,20,8,5,12,21] spall C, N, Ne, A, Kr, Xe;[22] Be-γ-p;[9,11,23] B-n-α;[24] B-γ-2p., B-γ-2pn[11]	^{8}Li
		Be-d-2p;[25] B-p-3p, B-d-3pn;[25] B-γ-2p;[11] C-d-4pn, C-p-4p;[25] C-p-4p[26]	^{9}Li
	 ^{20}Na β⁺ ^{20}Ne >6·8 <10·8 ^{16}O + α 0 27	Ne-p-n;[27] Na-γ-3n[28,11]	$^{20}_{11}$Na

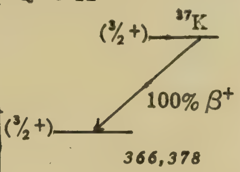
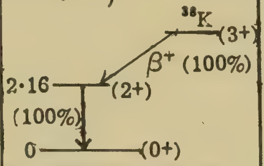
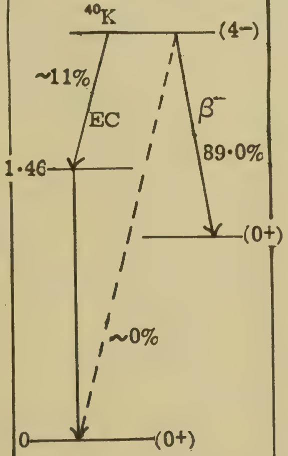
Refs. p. 2472

Isotope	Class and identification	Percent abundance	Type of decay	Half-life	Radiation energy, MeV. Particles
^{21}Na	A excit[30]		β^+[31] γ[367]	22·8 s;[32] 23 s[30] 23·0[365] 21·6[366]	2·50 spect;[32] 2·53 spect[33] 2·16 (2·2%)[367] 2·51 (97·8%)[367]
^{22}Na	A chem, excit[36]		β^+ 89·86%[37] EC[37] 10·2%	2·60 y;[38] 2·8 y[39] 2·58[368]	0·542 spect;[40] ~1·8 (0·06%) spect;[41] ~1·8 (0·004%) cl ch;[42] others[43,44] 0·544[369]
^{23}Na		100[1]			
^{24}Na	A chem, excit[55,56]		β^-[56]	15·06 h;[57] 15·04 h;[58] 15·10 h;[59] 15·0 h[60,61] 14·96[371] 15·00[372]	1·390 spect, coinc;[62,63] 1·4 spect;[64] 4·17 (0·003%), no 5·5 β^-, spect;[65] lim 4·15 β^-, 0·01% spect;[66] others[67] 0·28 (0·04%)[369] from γ-ray 1·391 (100%) weighted average[369]
^{25}Na	B excit[100]		β^-[100]	58 s;[101] 62 s;[102,88,100] 60 s[103] 60 s[374,375]	3·7 (~55%), 2·7 (~45%) abs;[101] 3·4 abs;[104] 3·3 abs;[103] 2·2(6·5%), 2·82(28·5%) 3.80 (65%) adopted values[369]

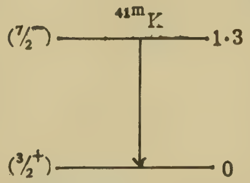
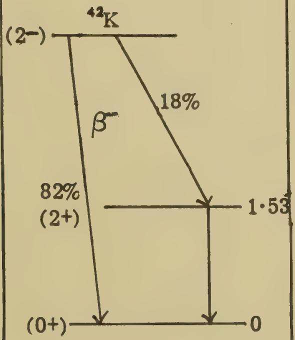
Refs. p. 2472

Radiation energy, MeV. γ-transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
no γ[32] 0·347 (2·2%)[367]	 ^{21}Na (2·2%) β^+ (97·8%) 0·35 0 β^+ 367	^{20}Ne-p-γ;[34] Ne-p-n;[30] Ne-d-n;[31] Mg-p-α;[32] ^{24}Mg-p-α[35]	^{21}Na
1·2736[370] 1·277 spect;[45] 1·3 spect;[44] others[46]	Q_{β}^{+} 2·84[47] ^{22}Na, I = 3[2]  ^{22}Na (3+) β^+ 89·8% EC 10·2% 1·274 (2+) ~100% β^+ 0·06% 0 (0+) 369	F-α-n;[36,43,48] Ne-d-n;[43] ^{21}Ne-p-γ;[34] Na-n-2n;[49,50] Mg-d-α;[43,45] spall Mg, ^{25}Mg, ^{26}Mg,[51] Fe,[52] Cu[53]	^{22}Na
	^{23}Na, I = $\frac{3}{2}$[2]		^{23}Na
γ_1 1·3679, γ_2 2·7535 spect;[68] γ_1 1·380, γ_2 2·758 spect;[62] 1·380, 2·765 spect;[69] γ_2 (e/γ 3×10^{-6});[70] 2·748 spect;[71] 2·755 spect;[72] γ_1 (coinc with γ_2) spect, β-γ, γ-γ coinc;[73] coinc abs;[74] 3·7 (0·04%) D-γ-p ion ch;[75] ~4 (0·05%) spect;[65] others[46,76-82] Weak high energy γ-rays[373]	Q_{β}^{-} 5·53[47] ^{24}Na, I = 4[83]  ^{24}Na β^- 0·04% 5·22 (3+) 100% 0·04% 4·12 (4+) 0·003% ~100% < 0·0008% 1·368 (2+) ~100% (0+) 0 369	Na-d-p;[56,84] Na-n-γ;[85,86] Mg-d-α;[87] Mg-n-p;[85] Mg-γ-p;[88-90] Al-n-α;[85,91] Al-d-pα;[92,93] Al-γ-n2p;[88,90,94] Al-p-3pn;[95] Si-γ-n3p (?);[88] spall Al,[96] Fe,[52] Cu,[53,97] Sn;[98] spall fission Cu,[98] U[99]	^{24}Na
>0·5 (weak) abs[101] 0·40, 0·58, 0·98, 1·61, 1·96[376]	Q_{β}^{-} 3·7[101] Suggested scheme[369]	Mg-γ-p;[104,88,90] Mg-n-p;[104,101] Al-γ-2p[88,102,90,94]	^{25}Na

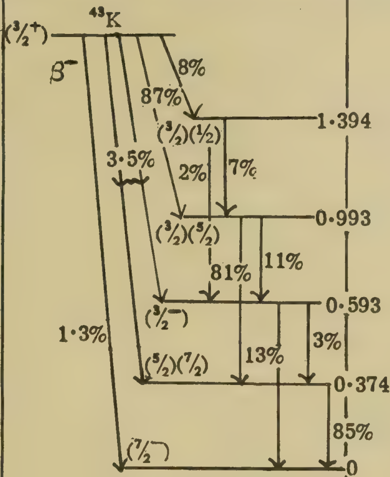
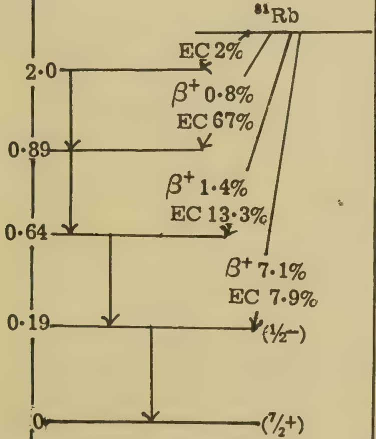
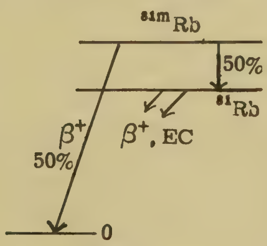
Isotope	Class and identification	Percent abundance	Type of decay	Half-life	Radiation energy, MeV. Particles
$^{37}_{19}$K	C excit[105]		β^+ [106]	1·23[377] 1·15[366] 1·20[378] 1·3 s;[105] 1·2 s[106]	4·6 scint spect[106] 5·15[366] 5·10[378]
^{38}K	A chem, cross bomb[107,108]		β^+ [107]	7·7 m;[107, 109,110, 379] 7·5 m;[111] 7·6 m[102] 7·67 m[380]	2·8 spect;[110] 2·5 abs;[111] others[109] 2·68[379] no 4·9 β^+ [379]
^{39}K		93·10;[1] ^{39}K/^{41}K variations[119]			
^{40}K	A chem;[120,121] chem, mass spect[122]	0·0118[1]	β^- 89%, EC 11%;[123] β^- ~88%, EC (K) ~12%;[124] β^- ~93%, EC (K) ~7%;[125] assuming EC/γ = 1, β^- 90%, EC 10%;[126,127] β^- 91%, EC 9%;[124] β^- 89%, EC 11%;[128] β^- 94%, EC 6%;[129] β^- 89·05% EC 10·95%	$t\beta$- spact (uncorr. for EC): 1·32×10^9 y;[133,134] 1·26×10^9 y;[135,136] 1·29×10^9 y;[126] 1·49×10^9 y;[137,127 138] 1·42×10^9 y;[124] others[139-141] $t_{1/2}$ 1·2×10^9 y calc from average $t\beta$- and EC/β^- [47]	1·33 spect;[142] 1·36 spect;[143] 1·36 scint spect;[144] 1·35 spect coinc;[145] 1·41 abs;[146,67] 1·28 scint spect[138] 1·321 least squares adjustment of ^{40}A and ^{40}K masses[369] 28·0 β's per gm. K Average of many determinations[369]

Radiation energy, MeV. γ-transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
	Q^+ 6·12[369]  *366,378*	K-γ-2n[105,106] Ca-p-α[366,377,378]	$^{37}_{19}$K
2·16 scint spect;[112] ~2·1 abs sec[111]	Q^- 4·81[47] (see also *113,114*)  ^{38}K (3+) β^+ (100%) 2·16 (2+) (100%) 0 (0+)	Cl-α-n;[107,109,108,111] K-n-2n;[115] K-p-pn;[112,110] K-γ-n;[116,114,102,90] Ca-d-α[107]	
	^{39}K, I = 3/2[2]		^{39}K
1·46 scint spect;[131, 147] 1·48 scint spect;[148] 1·47 scint spect;[149] 1·54 (with EC) abs, coinc;[146] 1·55 abs;[150] γ (with EC);[151,152] γ/β^- 0·12 sp act average of:[126,133, 134,138,140,153,154, 127] EC/γ ~1[155,124,152] 1·46 scint spect;[381]	Q_{β}^- 1·33[47] Q_{EC} 1·63[156,47] ^{40}K, I = 4[2]  ^{40}K (4−) ~11% EC β^- 89·0% 1·46 (0+) ~0% 0 (0+) *47*	natural source[120,121]	^{40}K

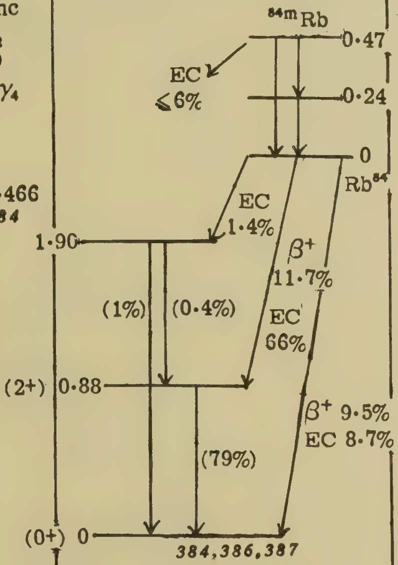
Isotope	Class and identification	Percent abundance	Type of decay	Half-life	Radiation energy, MeV. Particles
			adopted values[369] no β^+ (lim. 0·06%); [130] no β^+ (lim. 0·002%); [131] β^+ $\leqslant 0{\cdot}1\%$ [132]		
^{41m}K	A genet[157]		IT[157]	$6{\cdot}7 \times 10^{-9}$ s delay coinc[157]	
^{41}K		6·88[1]			
^{42}K	A chem, n-capt; chem, cross bomb[159,160]		β^-[161]	12·44 h;[162] 12·5 h;[163,60] 12·4 h;[107] 12·46 h;[382]	3·58 (75%), 2·04 (25%) spect;[162] 3·60, 1·9 spect;[164] 3·5 (~70%) (not coinc with γ), ~1·8 (~30%) abs, coinc[101]
^{43}K	B chem, excit[165]		β^-[165]	22·4 h[165]	0·465 (8·2%), 0·825 (87%), 1·24 (3·5%) 1·814 (1·3%) spect[383] 0·81, 0·24 spect, abs[165]

Radiation energy, MeV. γ-transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
~1·3 scint spect[157]	 157,158	daughter ^{41}A[157]	^{41m}K
	^{41}K, I=$\frac{3}{2}$[2]		^{41}K
1·51 spect;[162] 1·50 spect;[164] 1·5 (17%) scint spect[163]	$Q\bar{\beta}$ 3·6[47]  ^{42}K (2−) 18% β− 82% (2+) 1·53 (0+) 0 1	A-α-pn;[165] K-d-p;[107] K-n-γ;[85,107,86] Ca-n-p;[159,107] Sc-n-α;[160,107,101] spall Co,[166] Cu;[97] daughter ^{42}A[167]	^{42}K
0·220 (3%), 0·371 (85%), 0·388 (7%) 0·394 (11%), 0·591 (13%), 0·614 (81%), 1·005 (2%), scint spect[383] ~0·4 abs[165]	(For Diagram see next page)	A-α-p[165]	^{43}K

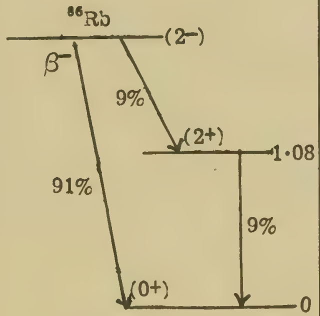
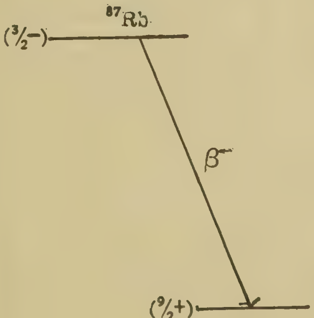
Isotope	Class and identification	Percent abundance	Type of decay	Half-life	Radiation energy, MeV. Particles
^{43}K					
^{44}K	A chem, excit[168]		β^- [165]	22·3 m[369] 18 m[168]	Many β-energies scint spect[369]
$^{81}_{37}$Rb	A chem, mass spect[170]		EC 87%, β^+ 13% [171] EC 90·7% [369] β^+ 8·3%	4·7 h[171, 384]	0·990 spect[171] 0·325, 0·575, 1·05 spect[384]
^{81m}Rb	B chem, genet[384]		β^+ 50% IT 50% [384]	31·5 m[384]	1·4 spect[384]

Radiation energy, MeV. γ-transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
	 ^{43}K ($\frac{3}{2}^+$) β^- 8% 87% 1·394 ($\frac{3}{2}$)($\frac{1}{2}$) 3·5% 2% 7% 0·993 ($\frac{3}{2}$)($\frac{5}{2}$) 81% 11% 0·593 ($\frac{3}{2}^-$) 1·3% 3% ($\frac{5}{2}$)($\frac{7}{2}$) 13% 0·374 85% ($\frac{7}{2}^-$) 0 369		^{43}K
Many γ-energies scint spect[369]	Complex scheme[369]	Ca-n-p[168,169]	^{44}K
0·95 abs[171] 0·253, 0·450, 1·1 spect[384]	 ^{81}Rb EC 2% 2·0 β^+ 0·8% EC 67% 0·89 β^+ 1·4% EC 13·3% 0·64 β^+ 7·1% EC 7·9% 0·19 ($\frac{1}{2}^-$) 0 ($\frac{7}{2}^+$) 369, 384	Br-α-n;[170,171] parent ^{81}Kr[171] Br-α-2n[170]	$^{81}_{37}$K
0·085 spect conversion in Rb[384]	 ^{81m}Rb 50% ^{81}Rb β^+ 50% β^+, EC 0 384	Br-α-2n[384] parent ^{81}Rb, ^{81}Kr	^{81m}Rb

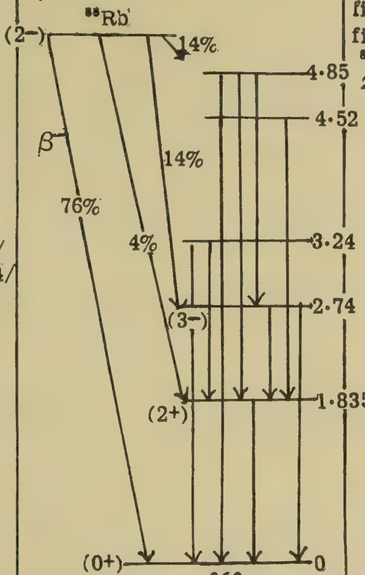
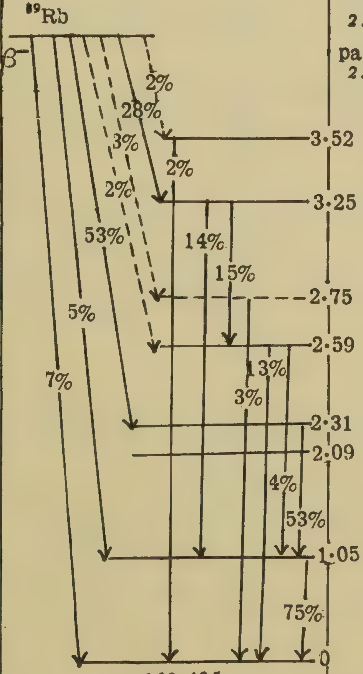
Isotope	Class and identification	Percent abundance	Type of decay	Half-life	Radiation energy, MeV. Particles
^{82}Rb	A chem, genet[172]		β^+ 96·2% [369] EC 3·8% β^+ [172]	1·25 m[172]	2·8 abs[172]
^{82m}Rb	A chem;[173] chem, mass spect[170]		EC 94%, β^+ 6%; [171] EC 79% β^+ 21% [385]	6·3 h[171]	0·775 (76%), 0·175 (24%) spect;[174] 0·670 spect;[171] 0·800 spect;[385]
^{83}Rb	A chem, mass spect[171]		EC[171]	83 d;[175] 107 d[171]	
^{84m}Rb	B chem;[173] chem, excit [176]		IT, EC (weak); [177] EC[176] EC $\leqslant$ 6% [384]	23 m;[176] 20 m;[173] 20·5 m[384]	
^{84}Rb	A chem, cross bomb[178] chem, mass spect[171]		EC, β^+, β^- (?); [171,179] EC/β^+ ~13;[171] β^+/β^- ~6·2[179]	34 d;[171] 38 d;[179] 33 d[386]	β^+: 1·629 (39%), 0·822 (58%), 0·373 (?) (3%) spect;[174] 1·5 spect;[171] 1·3 abs;[179] β^+ 0·79 (11·7%), 1·63 (9·5%), β^+ 0·908 (2·7%) spect;[384,386]
^{85m}Rb	A genet[180]		IT[180]	$0{\cdot}9\times10^{-6}$ s delay coinc[180]	

Radiation energy, MeV. γ-transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
		daughter ^{82}Sr[172]	^{82}Rb
0·188, 0·248, 0·322, 0·390, 0·423, 0·465, 0·558, 0·610, 0·690, 0·768, 0·818, 1·020, 1·314, 1·464 spect conv, spect[174]		Br-α-n;[173,170,171] Kr-d-2n;[173] not daughter ^{82}Sr (lim 0·01%)[172]	^{82m}Rb
~0·45, ~0·15 spect conv[175]		Br-α-2n;[171] daughter ^{83}Sr;[175] parent ^{83m}Kr[175]	^{83}Rb
γ_1 0·463 (not coinc with γ_2 or γ_3), γ_2 0·239, γ_3 ~0·239 (coinc with γ_2), γ_4 0·890 ($\gamma_1/\gamma_4 \approx 7$) scint spect, γ-γ coinc[177] 0·217, ~0·239, 0·466 γ-rays of Rb^{84} [384]	 ^{84m}Rb 0·47 0·24 0 Rb^{84} EC ≤6% EC 1·4% β^+ 11·7% EC 66% β^+ 9·5% EC 8·7% 1·90 (1%) (0·4%) (2+) 0·88 (79%) (0+) 0 384,386,387	Br-α-n;[173] Rb-n-2n[176,177]	^{84m}Rb
0·890 scint spect, spect conv;[174] 0·85 abs;[171] 0·8 abs;[179] 0·879 (79%), 1·01 (0·4%), 1·90 (1·0%) scint spect[387]		Br-α-n;[171,179] Kr-α-pn, Kr-s-2n;[179] Rb-n-2n;[178] Sr-d-α[178]	^{84}Rb
0·513 spect, spect conv[181,180]		daughter ^{85}Sr[180]	^{85m}Rb

Isotope	Class and identification	Percent abundance	Type of decay	Half-life	Radiation energy, MeV. Particles
^{85}Rb		72·15[1]			
^{86m}Rb	B chem, excit, n-capt[184]		IT, no EC;[185] EC[184]	0·99 m;[185] 1·06 m[184]	
^{86}Rb	A chem, n-capt;[186] chem, excit [187]		β^-;[187] no β^+ (lim 0·002%) [188] no EC (lim 0·04%) [185]	19·5 d[187] 18·64 d[388] 18·66 d[389] 18·68 d[382] 18·7 d[390]	β_1 1·777, weighted average of [189,190,191, 192,193,194,195,391, 392,393,394] β_2 0·717 β-γ,[390] 0·700 spect,[192] 0·711 spect,[391] 0·720 spect,[194] 0·694 spect,[195] 0·680 spect,[392] 0·715 spect,[393,394] average percentage 9%[363]
^{87}Rb	A chem;[120,121] chem, genet;[202,203] chem, mass spect[204]	27·85[1]	β^- [120, 121]	$6{\cdot}0\times10^{10}$ y sp act;[205, 206,207, 208] $6{\cdot}4\times10^{10}$ y sp act;[209] $6{\cdot}2\times10^{10}$ y sp act;[210,397, 398] $7{\cdot}6\times10^{10}$ y ([211], calc from [210]); $6{\cdot}3\times10^{10}$ y yield;[212] $5{\cdot}8\times10^{10}$ y sp act[213] $4{\cdot}3\times10^{10}$ y sp act[399] $5{\cdot}07\times10^{10}$ y sp act;[400] $5{\cdot}0\times10^{10}$ y yield and mass spect;[401] $4{\cdot}6\times10^{10}$ y chem, yield[402] $4{\cdot}7\times10^{10}$ y sp act;[396] $5{\cdot}25\times10^{10}$ y sp act[403]	0·275 spect;[210] scint spect;[208] 0·270 scint spect;[214] others[215-219] 0·272 scint spect[396]

Radiation energy, MeV. γ-transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
	^{85}Rb, $I = \frac{5}{2}$ [2]	fission U (mass spect)[183]	^{85}Rb
0·57 scint spect;[185] 0·78 abs[184]		Rb-n-γ, Rb-n-2n[184]	^{86m}Rb
1·076 spect;[193] 1·081 spect;[189,391] others[46] 1·08 (8·9%)[395] 1·055 spect[393] 1·080 spect[392] 1·083 spect[195]	^{86}Rb, $I = 2$[196] Q_{β^-} 1·8,[189] 1·777[369]  ^{86}Rb (2−) β− 9% (2+) 1·08 91% 9% (0+) 0 369	Rb-n-γ;[186,197] Rb-γ-n;[198] Sr-d-α;[187] spall-fission Bi,[199,200] U;[99] fission U[201]	^{86}Rb
no γ[210,209,208]	^{87}Rb, $I = \frac{3}{2}$ [2] Q_{β^-} 0·27,[210] 0·273[369]  210,209	natural source;[120,121] fission U (mass spect);[183] parent ^{87}Sr (mass spect)[202,203]	^{87}Rb

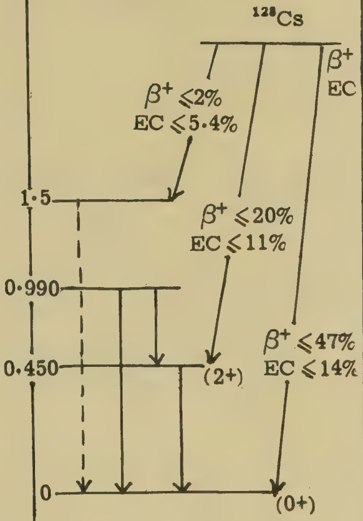
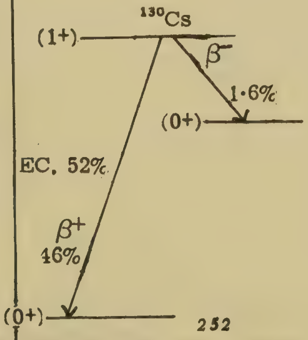
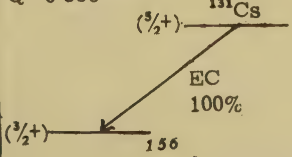
Isotope	Class and identification	Percent abundance	Type of decay	Half-life	Radiation energy, MeV. Particles
^{88}Rb	A chem;[186] chem, genet [220-222]		β^-[222]	17·8 m;[221, 223] 17·7 m;[224] 17·5 m;[225] 18 m[226,186]	5·30 (78%), 3·6 (13%), 2·5 (9%) spect;[224] 5·13 (66%), 3·29 (19%), 2·0 (15%) spect;[223] 5·20 (∼66%), 3·6 (∼17%), 1·8 (∼17%) abs[227]
^{89}Rb	A chem, genet [221,232]		β^-[221]	15·4 m;[221] 15·5 m;[226] 14·9 m[405]	4·5 abs[233] calc from;[221] 3·8 abs[221] 2·81 (6%), 3·92 (11%) scint spect[405]

Radiation energy, MeV. γ-transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
2·8, 1·86, 0·90 spect;[223] γ_1 3·0 γ_2 1·7 (γ_1/γ_2 ~1/10) abs sec, β-γ coinc[227] γ_1 4·87, γ_2 3·68, γ_3 3·52, γ_4 3·24, γ_5 3·01, γ_6 2·68, γ_7 2·11, γ_8 1·850, γ_9 1·39, γ_{10} 0·908 ($\gamma_1/\gamma_2/\gamma_3/\gamma_4/\gamma_5/\gamma_6/\gamma_7/\gamma_8/\gamma_9/\gamma_{10}$) = (1·4/0·4/1·1/1·4/1·4/11/4·5/100/6/63) scint spect[404]	Q_{β^-} 5·30[224] 5·2[369]  ^{88}Rb (2−) 14% β^- 76% 4% 14% (3−) (2+) (0+) 4·85 4·52 3·24 2·74 1·835 0 369	Rb-n-γ,[186,115,197,86] fission Th,[228] Pa;[229] fission U, daughter ^{88}Kr[230,220,221,231,226]	^{88}Rb
γ[233] γ_1 3·52, γ_2 2·75, γ_3 2·59, γ_4 2·20, γ_5 1·55, γ_6 1·26, γ_7 1·05, γ_8 0·663 ($\gamma_1/\gamma_2/\gamma_3/\gamma_4/\gamma_5/\gamma_6/\gamma_7/\gamma_8$) = (2/3/13/14/4/53/75/15)[405]	Q_{β^-} = 3·92[405]  ^{89}Rb β^- 2% 28% 3% 2% 2% 53% 14% 15% 5% 7% 13% 3% 4% 53% 75% 3·52 3·25 2·75 2·59 2·31 2·09 1·05 0 369,405	fission U, daughter ^{89}Kr;[221,232,226,234,235] parent ^{89}Sr[221,231,226,234]	^{89}Rb

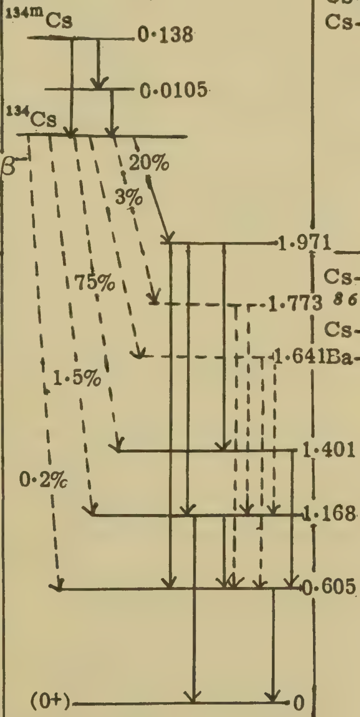
Isotope	Class and identification	Percent abundance	Type of decay	Half-life	Radiation energy, MeV. Particles
^{90}Rb	A chem, genet 236		β^- [236]	2·74 m[236] 2·90 m[406]	5·7 abs,[236] β_1 6·59, β_2 5·81, β_3 4·4, β_4 2·21, β_5 1·2 scint spect[406]
^{91}Rb	A chem, genet 236		β^-[236]	1·67 m;[236] [short] 237,235, 239,238, 240	4·6 abs[236] spectrum complex[236]
^{91m}Rb	A chem, genet 236		β^- [236]	14 m[236]	3·0 abs[236] spectrum complex[236]
^{92}Rb	D chem, genet 231		β^- [231]	80 s;[231] [short] 235,238	
^{93}Rb	F genet[242,235]		[β^-][242]	[short][235, 238,237, 242,234]	
^{94}Rb	F genet[234,243]		[β^-][234, 243]	[short][238, 234,243]	
^{95}Rb	F genet[237]		[β^-][237]	[short][237]	
^{97}Rb	F genet[238]		[β^-][238]	[short][238]	
$^{123}_{55}$Cs	B chem, genet 408		β^+ [408]	6 m[408]	
$^{125}_{55}$Cs	A chem, mass spect[245]		β^+ [245] EC	45 m[245]	2·03 spect[245]
^{126}Cs	A chem, mass spect[409]		β^+ 85% EC 15% 409,369	1·6 m[409]	3·84 scint spect[409] β_1 3·84 (59%); β_2 ~3·4 (31%)[369]
^{127}Cs	A chem, mass spect[246]		β^+ [246] $<10\%$[369] EC $<90\%$ 369	5·5 h[246] 6·1 h[410, 411] 6·25 h[408]	1·2 spect, abs[246] β_1 1·063, β_2 0·685 spect[408] β_1 1·021, β_2 0·677 spect[411]

Radiation energy, MeV. γ-transitions	Disintegration energy and scheme	Method of production and genetic relationships	isotope
γ[236] 23 possible γ-rays[406]	scheme complex[406]	fission U, daughter ^{90}Kr; parent ^{90}Sr[236-238]	^{90}Rb
γ[236] 0·1 scint spect[407]		fission U, daughter ^{91}Kr, parent ^{91}Sr;[236] ancestor ^{91}Y[237,240]	^{91}Rb
γ[236]		fission U, daughter ^{91}Kr, parent ^{91}Sr[236]	^{91m}Rb
		fission U, daughter ^{92}Kr;[238] ancestor ^{92}Y[231,240,241,234,238]	^{92}Rb
		fission U, daughter ^{93}Kr;[235,238,237] ancestor ^{93}Y[242,234,235]	^{93}Rb
		fission U, daughter ^{94}Kr; ancestor ^{94}Y[234,243,238]	^{94}Rb
		fission U, daughter ^{95}Kr; ancestor ^{95}Zr[237]	^{95}Rb
		fission U, daughter ^{97}Kr; ancestor ^{97}Zr;[238] fission ^{235}U, Pu[246]	^{97}Rb
		parent ^{123}Xe[408]	$^{123}_{55}$Cs
0·112 scint spect[245]		I-α-6n,[245] parent 18 h; ^{125}Xe and 55 s; ^{125}Xe[245]	$^{125}_{55}$Cs
0·385 (38%) scint spect[409]	Q^{+}_{β} 5·1[369]	daughter ^{126}Ba[409]	^{126}Cs
γ_1 0·406, γ_2 0·363, γ_3 0·285, γ_4 0·196, γ_5 0·169, γ_6 0·1246, spect[408] γ_1 0·411, γ_2 0·286, γ_3 0·124 spect[411]	Q^{+}_{β} 2·085[369]	I-α-4n;[246] parent ^{127}Xe;[246] daughter ^{127}Ba[247]	^{127}Cs

Isotope	Class and identification	Percent abundance	Type of decay	Half-life	Radiation energy, MeV. Particles
^{128}Cs	B chem, genet [248]		β^+, EC[247] EC ⩽ 30% [369]	3·8 m;[247] 3·1 m;[248] 3·9 m[412]	3·0 abs[249,250,247] β_1 3·0, β_2 2·5, β_3 1·5 ($\beta_1/\beta_2/\beta_3$ = 70/30/3) spect[413]
^{129}Cs	A chem, mass spect[246]		EC, no β^+ [246, 411]	31 h[246] 30·1 h[411]	conv: ~0·3 abs[246]
^{130}Cs	A chem;[251] chem, excit;[252] chem, mass spect[245]		β^+, EC, β^- (β^+/β^- 27·5) [252]	30 m;[252] ~30 m[251, 246]	β^+: 1·97 spect;[252] β^-: 0·442 spect[252]
^{131}Cs	A chem, genet; [253] chem, mass spect[254]		EC, no β^+ [255-257]	9·6 d;[258] 10·2 d;[253] 10·0 d;[259] 9·9 d[414]	

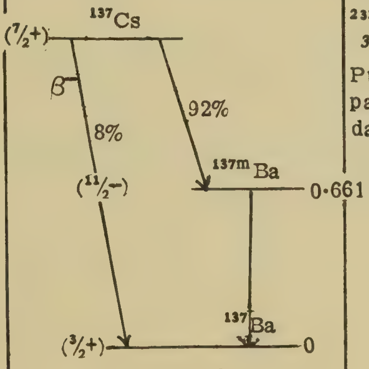
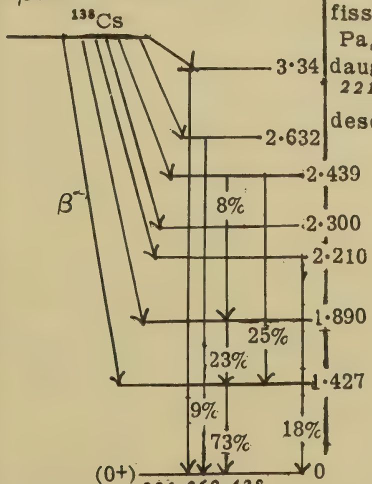
Radiation energy, MeV. γ-transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
γ_1 0·980, γ_2 0·445 scint spect[413]	Q^+ 4·0[369]  ^{128}Cs β+ EC β+ ≤2% EC ≤5·4% 1·5 β+ ≤20% EC ≤11% 0·990 β+ ≤47% EC ≤14% 0·450 (2+) 0 (0+)	daughter ^{128}Ba[248,247]	^{128}Cs
~0·5 abs[246] γ_1 0·585, γ_2 0·545, γ_3 0·411, γ_4 0·371, γ_5 0·315, γ_6 0·283, γ γ_7 0·174, γ_8 0·092 γ_9 0·040 scint spect[411]	Q^+ 1·2[369] scheme complex[369]	I-α-2n;[246] daughter ^{129}Ba[249,250]	^{129}Cs
no γ,[252] Xe K-x[252]	Q_{β}^- 0·442, Q_{β}^+ 2·99[252]  ^{130}Cs (1+) β− 1·6% (0+) EC, 52% β+ 46% (0+) 252	I-α-n[251,246,252]	^{130}Cs
no γ[256,253,257,260] Xe K-x[256,259,258,253,255] ~0·1 abs conv, abs[259,258]	Q^+ 0·355[369] 	I-α-γ;[261] daughter ^{131}Ba;[253,259,258,256] not parent ^{131m_2}Xe;[256] parent (?) ^{131m_2}Xe[262]	^{131}Cs

Isotope	Class and identification	Percent abundance	Type of decay	Half-life	Radiation energy, MeV. Particles
^{132}Cs	A chem, excit [263]		EC[263] no β^+, <2%; no β^-, <5%[416]	7·1 d;[263] 6·2 d[415]	
^{133m}Cs	A genet[265]		IT[265]	$6{\cdot}0\times10^{-9}$ s delay coinc[265]	
^{133}Cs		100[266 1]			
^{134m}Cs	A chem; n-capt; [87,267] chem, excit, n-capt[268]		IT[164, 269,270]	3·2 h;[271] 3h[268]	
^{134}Cs	A n-capt;[275] chem, n-capt, excit[268]		β^-,[268] no EC (lim 4%);[276] no EC (lim 5%);[277] no β^+ (lim 0·009%)[188]	2·3 y;[278] 1·7 y;[268] 2·19 y;[368] 2·07 y;[422] 2·15 y[423]	0·648 (75%), 0·09 (25%) spect;[279] 0·65 spect;[276] 0·66 (~72%), 0·09 (~28%) spect;[280] 0·676, 0·640, ~0·08 (~24%) spect;[274] 0·60, 0·09 abs, β-γ coinc abs;[281] others[282,268,164,283] Values on accepted decay scheme[369] β_1 1·45 (0·2%), β_2 0·89 (1·5%), β_3 0·652 (75%), β_4 0·41, β_5 0·28 (3%), β_6 0·086 (20%); refs include 424,425,426,427, 418,417
^{135m}Cs	A genet[265]		IT[265]	$2{\cdot}8\times10^{-10}$ s delay coinc[265]	

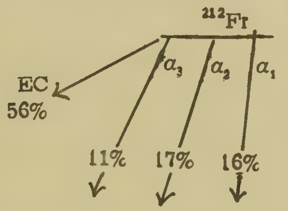
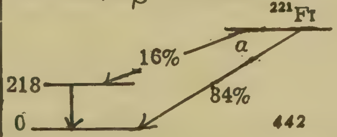
Radiation energy, MeV. γ-transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
0·668 scint spect;[264] 0·62 abs, abs conv[263] γ_1 1·30, γ_2 1·20, γ_3 1·08, γ_4 0·77, γ_5 0·670; ($\gamma_1/\gamma_2/\gamma_3/\gamma_4/\gamma_5$) = (1/0·6/0·6/?/100) scint spect[416]	Q^+ 1·9[369] Q^- 1·2[369]	Cs-n-2n;[263,264] Cs-p-pn[416]	^{132}Cs
~0·081 (e_K/γ 1·8, K/L+M 6·0) scint spect, β-γ delay coinc[265]		daughter ^{133}Xe[265]	^{133m}Cs
	^{133}Cs, I = 7/2 [2]		^{133}Cs
0·0105 (α ~200)[428] 0·128 (K/L.M ≈ 64·3/100/18·6) spect conv;[270] 0·128 (e_K/γ 2·2) scint spect;[272] 0·128 (L_{II}/L_{III} ~1) spect conv;[273] others;[164,269,271] 0·1271 spect conv[428]	 ^{134m}Cs 0·138 0·0105 ^{134}Cs β^- 20% 3% 75% 1·5% 0·2% 1·971 1·773 1·641 1·401 1·168 0·605 (0+) 0	Cs-n-γ;[87,267,268,86] Cs-d-p[268]	^{134m}Cs
Numerous results energies on accepted decay scheme[369] include; γ_1 1·367, γ_2 1·168, γ_3 1·038, γ_4 0·801, γ_5 0·7964, γ_6 0·6047, γ_7 0·570, γ_8 0·563, γ_9 0·473 refs [274,276,280,284,285,286,417,418,419,420] γ_1 1·37 (3·3%), γ_2 1·17 (2·5%), γ_3 1·04 (2%), γ_4 0·80 (90%), γ_5 0·605 (98%), γ_6 0·57 (24%), γ_7 0·48 (1·3%) spect[421]	^{134}Cs, I = 4[295]	Cs-n-γ;[275,197,268,86] Cs-d-p;[268] Ba-d-α[296]	^{134}Cs
0·248 (K/L 7·0) spect conv, scint spect, β-γ delay coinc[265]		daughter ^{135}Xe[265]	^{135m}Cs

Refs. p. 2472

Isotope	Class and identification	Percent abundance	Type of decay	Half-life	Radiation energy MeV. Particles
^{135}Cs	A chem, genet;[297] chem, mass spect[298]		β^- [297]	2·0 × 10^6 y [429] 3·0 × 10^6 y sp act;[299] 2·1 × 10^6 y yield[297]	0·21 abs;[297] $\sim$0·19 abs[299]
^{136}Cs	A chem;[300,301] chem, excit [302]		β^- [301]	13·7 d[302] 12·9 d[430]	0·35 abs;[302] 0·28 β-γ coinc abs; [303] β_1 0·657 (7·4%) β_2 0·341 (92·6%) spect [430]
^{137}Cs	A chem, genet; [308] chem, mass spect[309,298]		β^- [308]	33y;[310, 183,431] 30·0 y; [432] 26·6 y [436]	β_1 0·523 spect;[311] β_1 0·51 (92%), β_2 1·17 (8%) spect;[312] β_1 0·521, β_2 $\sim$1·2 spect;[313] β_1 0·518, β_2 $\sim$1·18 spect;[314] others[315-317] β_1 0·514 (92·4%), β_2 1·18 (7·6%) spect;[433] β_1 0·51 (95·2%), β_2 $\sim$1·2 (4·8%) scint spect[434] β_1 0·519 ($\sim$97%), β_2 1·18 ($\sim$3%) spect[435]
^{138}Cs	A chem;[222,230] chem, mass spect[329]		β^- [222]	32·9 m; [330] 33m;[228, 222] 32 m;[328, 221] 32·2 m; [437] 32·1 m [438]	3·40 (coinc with 1·4 γ), $\sim$2·9, $\sim$2·0 spect, β-γ coinc abs;[331] 2·68 spect;[329] 2·65 abs ([233], calc from [221])

Radiation energy MeV. γ-transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
no γ[297,299]	^{135}Cs, I = 7/2 [2]	daughter ^{135}Xe;[297] fission U[299,183]	^{135}Cs
~0·9 abs;[302] 1·2 β-γ coinc abs;[303] two γ's[302] 13 γ's scint spect spect, conv[430]		La-n-α;[263,302] spall-fission Th[304] U;[101] fission Th,[305] ^{233}U,[306,307] ^{235}U,[307,301] Pu[303,301]	^{136}Cs
with ^{137m}Ba; 0·6616 cryst spect;[318] others[319,320,315,321,322,323,217,313,314]	^{137}Cs, I = 7/2 [2] Q_{β^-} 1·2,[47] 1·176[369]  ^{137}Cs (7/2+) β^- 8% 92% ^{137m}Ba 0·661 (11/2−) ^{137}Ba (3/2+) 0 315,312	spall-fission Th;[304] fission Th,[305] U,[324,298,310,183] ^{233}U,[306,307] ^{235}U,[307] Pu;[325] parent ^{137m}Ba;[326,317] daughter ^{137}Xe[327,328]	^{137}Cs
γ_1 0·463, γ_2 0·98, γ_3 1·44 (coinc with γ_1 and γ_2) spect conv, scint spect, β-γ, γ-γ coinc;[331] 1·2 abs;[328,330] 14 γ-rays[438,439] most abundant; γ_1 2·63 (9%), γ_2 2·21 (18%), γ_3 1·426 (73%), γ_4 1·01 (25%), γ_5 0·550 (8%), γ_6 0·4626 (23%)[438]	Q_{β^-} 4·84,[331] 4·83[369]  ^{138}Cs β^- 3·34 2·632 2·439 8% 2·300 2·210 1·890 25% 23% 1·427 9% 73% 18% (0+) 0 331,369,438	Ba-n-p;[332] fission Th,[228,241] Pa,[229] U;[230,231] daughter ^{138}Xe;[231,221,332] descendant ^{138}I[332]	^{138}Cs

Isotope	Class and identification	Percent abundance	Type of decay	Half-life	Radiation energy, MeV. Particles
^{139}Cs	A chem, genet 222,230		β^- 222	9·5 m;^{334} 10 m;^{228,230} 7 m^{231}	4·3 absorp^{440}
^{140}Cs	A chem;^{231} chem, genet^{334}		β^- 231	66 s^{334}	
^{141}Cs	F genet^{235}		$[\beta^-]^{235}$	short;^{235,238,239}	
^{142}Cs	D chem, genet 335		β^- 335	~1 m^{335}	
^{143}Cs	F genet^{235}		$[\beta^-]^{235}$	short^{235,238,239}	
^{144}Cs	F genet^{237}		$[\beta^-]^{237}$	short^{237,238}	
$^{212}_{87}$Fr	A chem, genet; 336 chem, mass spect^{337}		EC 56%, α 44% 336	19·3 m^{336}	6·409 (37%), 6·387 (39%), 6·339 (24%) spect;^{338} 6·36 ion ch;^{339} α_1 6·342, α_2 6·387, α_3 6·342, $(\alpha_1/\alpha_2/\alpha_3 = 37/39/24)$ spect^{441}
^{217}Fr	E genet, decay charac^{340}		α^{340}		8·3 range emuls^{340}
^{218}Fr	B genet^{341,342}		α^{342}	5×10^{-3} s est^{342}	7·85 ion ch^{342}
^{219}Fr	A genet^{344}		α;^{344} β stable (cons energy) 47	0·02 s delay coinc^{342}	7·30 ion ch^{342}
^{220}Fr	A genet^{344}		α^{344}	27·5 s^{342}	6·69 ion ch^{342}
^{221}Fr	A chem ,genet 345,346		$\alpha^{346,345}$	4·8 m;^{347} 5 m^{346}	6·30 ion ch;^{345,348} 6·30 (~75%), 6·05 (~25%) ion ch^{347} 6·33 (84%), 6·12 (16%) spect^{442}

Radiation energy, MeV. γ-transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
>0·7 absorp[440]	Q^{-} 4·3[440]	fission Th,[228] U;[222, 230,231] daughter ^{139}Xe;[222, 230,241,231] descendant ^{139}I;[333] parent ^{139}Ba[222,230, 241,231,334]	^{139}Cs
		fission U;[231,334] parent ^{140}Ba[334]	^{140}Cs
		[daughter ^{141}Xe]; [235,238,239] [ancestor ^{141}La][235]	^{141}Cs
		fission U, parent ^{142}Ba[335]	^{142}Cs
		[daughter ^{143}Xe];[235, 238] [ancestor ^{143}Ce][235, 238]	^{143}Cs
		[saughter ^{144}Xe];[238] [ancestor ^{144}Ce][237 238]	^{144}Cs
	 ^{212}Fr EC 56% α_3 α_2 α_1 11% 17% 16% 369,441	spall Th;[336] parent ^{212}Em[336,337]	$^{212}_{87}$Fr
		descendant ^{225}Pa[340]	^{217}Fr
	Q_{α} 8·00, Q_{EC} 1·8 calc[343]	daughter ^{222}Ac, parent ^{214}At[341,342]	^{218}Fr
	Q_{α} 7·44[343]	daughter ^{223}Ac, parent ^{215}At[344,340,342]	^{219}Fr
	Q_{α} 6·81, $Q_{\bar{\beta}}$ 1·27 calc, Q_{EC} 0·89 calc[343]	daughter ^{224}Ac, parent ^{216}At[344,341,342]	^{220}Fr
0·220 spect conv, scint spect[349] 0·216 (14%) spect conv scint spect [442]	$Q\alpha$ 6·42, $Q_{\bar{\beta}}$ 0·24 calc[343]  442	daughter ^{225}Ac, parent ^{217}At;[346,345,348,347] daughter ^{221}Em[337]	^{221}Fr

Refs. p. 2472

Isotope	Class and identification	Percent abundance	Type of decay	Half-life	Radiation energy, MeV. Particles
^{222}Fr	A chem, genet ^{350}		β^- 99+% α 0·01–0·1%^{351}	14·8 m^{350}	
^{223}Fr (AcK)	A chem, genet ^{352,353}		β^-;^{354,355} α 4×10^{-3} %^{356} α 6×10^{-3} %^{443,444}	21 m^{352}	β^-: 1·2 cl ch^{354,353,357} α 5·34 range, emulsion^{443,444}

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Radiation energy, MeV. γ-transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
	Q_α 6·00 est, $Q_{\bar\beta}$ 1·98 calc. Q_{EC} 0·02 est[343]	spall Th, parent ^{222}Ra, ancestor ^{214}Bi[350,351]	^{222}Fr
0·09 abs;[358,359] ~0·330 (6%) abs, 0·0486 (27%) crit abs;[357] γ_1 0·31 (0·8%), γ_2 0·215 (3%), γ_3 0·080 (24%), γ_4 0·0489 (40%) scint spect[445]	Q_α 5·60 est, $Q_{\bar\beta}$ 1·19 calc [343] Q_α 5·44, $Q_{\bar\beta}$ 1·15	natural source, daughter ^{227}Ac, parent ^{223}Ra (AcX);[352,354, 353,360,359,355,357] parent ^{219}At[356]	^{223}Fr

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SECTION XCIX

THE USE OF RADIOACTIVE ISOTOPES OF THE ALKALI METALS IN CHEMICAL STUDIES

By C. B. AMPHLETT

Radioactive tracers are available for all the alkali metals except lithium; those most suitable from the viewpoint of half-life and radiation energy are given in Table I.

TABLE I.- ALKALI METAL ISOTOPES SUITABLE FOR USE AS RADIOACTIVE TRACERS

Nuclide	Mode of Production	Half-life	Radiation, MeV.	
			β	γ
^{22}Na	^{24}Mg(d,α) (cyclotron)	2·6 y.	0·54 (β^{+})	1·28
^{24}Na	^{23}Na(n,γ) (pile) ^{23}Na(d,p) (cyclotron)	15 h.	1·39	2·76 1·38
^{42}K	^{41}K(n,γ) (pile) ^{40}A(α,d) (cyclotron)	12·4 h.	3·58 2·04	1·51
^{86}Rb	^{85}Rb(n,γ) (pile)	19·5 d.	1·82 0·72	1·08
^{134}Cs	^{133}Cs(n,γ) (pile)	2·3 y.	0·66 0·09	0·561– 1·365
^{137}Cs	Fission-products	33 y.	1·2 0·51	0·66

Isotopes of all these elements can be produced by (n,γ) reactions in a nuclear reactor with yields up to tens or hundreds of millicuries per gram of the parent element. For sodium and potassium cyclotron-produced isotopes are also available and in many cases are more suitable, since higher specific activities may be attained by chemical separation, e.g. ^{22}Na can be obtained carrier-free in quantities up to 5 millicuries by bombarding a magnesium or magnesium oxide target and leaching out the activity with warm distilled water; yields of 0·3–1 microcuries/microamp.hr. are obtained at 8–16 MeV. Similarly, very high specific activities of ^{42}K are obtained by recoil in cyclotron-irradiations of argon gas, 1 millicurie/microamp.hr. being obtained with 40 MeV. α-particles; potassium-43 (22·4 h., β 0·25 and 0·8 MeV., γ 0·4 MeV.) is also obtained in this reaction.[1] Potassium-42 is also produced by the reaction ^{41}K(d,p), giving 350–500 microcuries/microamp.hr. with 12 MeV. deuterons; the reaction ^{44}Ca(d,α) gives a much lower yield but a higher specific activity.

Laboratories possessing small neutron sources can readily prepare tracer quantities of ^{42}K of high specific activity by either of the reactions ^{45}Sc(n,α) and ^{42}Ca(n,p);[1] its preparation by the reaction ^{41}K(n,γ) is complicated by the presence of sodium as impurity, leading to the production of ^{24}Na also, which is difficult to remove from the potassium because of the close similarity in chemical and nuclear properties. Cæsium-137 is readily available in fission-products, and is separated and marketed in a high degree of chemical and radiochemical purity. The fission yield is high (6·2%), but dilution with inactive ^{133}Cs and ^{135}Cs prevents attainment of the theoretical specific activity. It has been estimated that a specific activity of 25 curies/g. of cæsium sulphate should be attainable,[2] and such compact sources appear promising as radiotherapy units in the kilocurie range, since the material is readily available and the half-life is many times greater than that of ^{60}Co. They may also find uses in much larger sources (10^5–10^7 curies) for future industrial processes utilizing radiation.[3]

EXCHANGE STUDIES UTILIZING RADIOACTIVE ALKALI METALS

Because the alkali metals are strongly electropositive and form only ionic compounds, there is no possibility of studying simple homogeneous exchange reactions in solution for these elements. The one example involving an exchange of homogeneous type that has been studied concerns the partially associated anions of polyacrylic acid. The original theory, developed[4] to explain quantitatively the changes in pH and equivalent conductivity of polyacrylic acid solutions on dilution, assumed that the current was carried almost entirely by H^+ ions. Subsequent transport measurements on partially neutralized solutions, employing tracer Na^+ ion, showed, however, that up to 50% of the current could be carried by the polyacrylate ions, and that these were partially associated with the cation,[5] e.g. at 25% neutralization, 25% of the cations were associated with the polymeric anion, and 67% at complete neutralization. Similar results were obtained from measurements of the steady-state diffusion of tracer Na^+ as a function of neutralization.[6] The bound Na^+ ions can exchange with free Na^+ ions in solution, and the exchange rate may be found from transport measurements; good correlation between experiment and theory is obtained if two exchange processes are postulated, one slow and the other rapid.[8] It is suggested that the cations in the outer atmosphere of the polymer ion exchange rapidly, while those within the coiled polymeric anion exchange much more slowly; the distribution of the cations between these two groups has been calculated, although the figures are subject to considerable uncertainty. The exchange between 'bound' and free cations has been followed for both Na^+ and K^+ as a function of the many variables possible in this system.[9]

The diffusion and migration of cations within cation-exchange resins and membranes has also been studied.[10-13] The similarity between the mechanisms of diffusion and of electrical conductivity in the electromigration of Na^+ ions in a Nepton CR-51 cation exchange membrane[11] parallels the results obtained in other cases of solid diffusion described below. A similar agreement between conductivities and self-diffusion coefficients has also been found[14] for Na^+ ions in keratin; since the observed ionic mobilities are considerably less than those for aqueous solutions, the mechanism cannot involve diffusion in liquid contained in the pores of the keratin.

There has recently been an increased interest in the quantitative aspects of ion-exchange in clay minerals, and a thermodynamic treatment of such systems has been published.[15] Exchange experiments have been carried out involving the cation-pairs Cs^+/Ca^{2+},Cs^+/Sr^{2+},Cs^+/K^+,Cs^+/Na^+,K^+/Na^+,Cs^+/Li^+ and the clay minerals montmorillonite and attapulgite.[16-19] Employing tracer Cs^+ and Na^+ ions, thermodynamic equilibrium constants have been calculated and activity coefficients derived for the component ions on the mixed-ion clays; the kinetics of the exchange process have also been studied. Tracer Rb^+ and Cs^+ ions have also been employed[20-22] to study the uptake of ions by paper and their transportation under an applied potential difference. It has been found that Cs^+ ion is adsorbed by an ion-exchange mechanism, presumably involving free carboxyl groups in the cellulose molecule; the exchange is strongly pH-dependent,[21] as would be expected for a weak acid exchanger. From the uptake of rubidium it was calculated that in cellulose there are 125 glucose units to each carboxyl group,[20] and the capacity of the paper to take up rubidium and caesium decreases as the cation originally on the paper changes from lithium to potassium to hydrogen. Application of 10 kV. to a stack of papers with rubidium-loaded papers next to the anode, followed by counting the activity on the individual papers, showed that about 30% of the total current was carried by the diffusing ions.[22]

It is well known that carrier-free activity is readily absorbed from solution on to the walls of glass vessels, and may lead to considerable error in experiments in which a carrier is not added. Some work has been reported on the incorporation of Na^+ ions into soft glass,[23,24] in which two approaches were made. Clear glass was suspended in tracer-active Na^+ solutions, or alternatively tracer-active glass (prepared by neutron irradiation in the pile) was suspended in inactive solutions. A further refinement consisted in suspending clean glass in a solution containing ^{24}Na tracer, followed by washing and re-suspension in a solution of ^{22}Na tracer; this enabled the adsorption and desorption to be followed simultaneously, and showed moreover that there was a slow net loss of Na^+ to the solution due to slow dissolution from the glass. Glass pretreated with Ba^{2+}, H^+ or K^+ before neutron-irradiation was found to lose less Na^+ ion on leaching with water afterwards, but the figures suggest that the depth of surface accessible to ion-exchange is small compared with the amount dissolved. Autoradiographs of a glass treated with tracer-active Cs^+ solution showed an uneven distribution of activity, and uptake was inhibited by heating the glass almost to fusion before treatment. Exchange experiments in ·05 M-sodium carbonate solution showed an initial exchange of approximately one half of a monolayer in 2–3 hrs. at 25°C., five monolayers exchanging in this time at 90°C.; the relatively rapid initial rate decreased fivefold between pH 12 and pH 5. Preliminary flaming cleaned the surface better than did washing and degreasing, although the activation energy is unchanged ($\sim$ 10 kg.-cal.), suggesting that flaming exposes a greater number of the same type of centres. Presoaking with 9N-hydrochloric acid increased the activation energy to 13·5 kg.-cal., indicating greater ease of exchange with $-Si-ONa$ than with $-Si-OH$; this is probably due to the salt of the weak acid being more strongly ionized than the parent acid. The adsorbed Na^+ ions were removed by water very slowly at room temperature, and more quickly at higher temperatures.

SELF-DIFFUSION IN AQUEOUS SOLUTIONS

The self-diffusion of sodium ions in aqueous solutions of sodium halides has been measured over a wide range of concentrations (5×10^{-5}M. to 5M.) by a number of workers, using both capillary cell and sintered diaphragm techniques. It was found[25,26] that the latter method gave high values of the diffusion coefficient at low concentrations, owing to a surface transport process through the fine capillaries of the diaphragm, which limits the concentration range that can be studied: since the results at low concentration are important for theoretical purposes this is a serious limitation. In these determinations the disagreement between experimental values and those calculated from the Onsager–Fuoss limiting law amounted to several per cent, and similar deviations were found for the diffusion of Na^+ in sodium iodide solutions determined by this method.[27] Measurements by the capillary tube method[28,29] have shown that at low concentrations (<·04M.) the diffusion of Na^+ in sodium chloride solutions is in agreement with the limiting law, but the diffusion of Na^+ in sodium iodide solutions, although showing the expected concentration dependence in very dilute solutions, does in fact give an extrapolated value of D_0 at infinite dilution some 7% higher than the theoretical value and in good agreement with Adamson's figure.[27] The coefficient for iodide ion at infinite dilution agreed well with the theoretical value. These results have recently been critically reviewed by Adamson,[30] who presents fresh evidence regarding the comparative usefulness of the two experimental methods.

DIFFUSION IN SOLIDS

In measuring diffusion in solid systems the tracer-active substance is held in contact with the substrate, either by deposition on the surface or by sandwiching between two plates of the substrate, and maintained at the required temperature for a given time. The activity within the substrate is then measured as a function of depth, either by counting on thin sections or by dissolving to a given depth, and the diffusion coefficient is then calculated.

Much work has been done on the diffusion of alkali metal ions in alkali halide crystals; it has been directed chiefly towards a study of the solid state, and in particular towards the relation between diffusion and electrical conductivity. If these two processes occur by the same mechanism, then by the Einstein relationship we should expect to find that $V/D = e/kT$, where V is the ionic mobility under an applied field, D is the diffusion coefficient, and the other symbols have their usual meaning. This is found to be true for the migration of Na^+ in sodium chloride and sodium bromide crystals above 550°,[31,32] and for K^+, Rb^+, Cs^+ and Ag^+ in sodium chloride crystals above 575°C;[33,34] at lower temperatures a somewhat different relationship holds. Measurement of the diffusion coefficients in the latter system over the temperature range 600–750° show them to have a common activation energy of ~ 44 kg.-cal.mole^{-1}, the absolute value of D at any temperature increasing with increasing ionic radius. The increased migration under an applied field has been used[35] to demonstrate the separation of ^{22}Na and ^{24}Na in sodium chloride and potassium chloride crystals. Thin layers containing both species were deposited on single crystals and a field of 10 V. was applied for 20 hours, the system being held at 700°C. (NaCl) or 750°C. (KCl). At a depth of 1 mm. the enrichment in ^{22}Na was 10–20%, the ratio $^{22}Na/^{24}Na$ increasing from 1·2 to 1·7–1·8; rather smaller enrichments were found for compressed potassium chloride pellets, where there is some non-selective intergranular migration. Better enrichments have recently been obtained[36] by electromigration on paper, the ions migrating along a length of paper held under carbon tetrachloride to prevent disturbances due to evaporation. The paper was moistened with 0·04% sodium chloride solution, and a field of 5000 V. applied across 40 cm., giving a current of 1 ma. at 20°C. Under these conditions the ions traversed 280 cm. in 1¾ hours, after which the paper was cut into strips for counting. It was found that after this time the higher mobility of $^{22}Na^+$ resulted in a variation in the ratio ^{22}Na:^{24}Na from 0·28 to 1·83 over a length of 7 cm.

Radioactive sodium has also been used to determine rates of diffusion in simple glasses such as sodium and potassium silicates and simple soda–lime–silica glasses between 300 and 1100°C.[37] The log D–$(1/T)$ curves show pronounced inflexions which are interpreted in terms of structural changes and alterations in degrees of freedom within the systems on cooling.

Self-diffusion of sodium in the solid state has been measured, using two cylinders of clean sodium metal, one inactive and the other active, pressure-welded together;[38-40] the rate was decreased by hydrostatic pressure, and showed no discontinuity on passing through the melting-point. Tracer sodium metal for this experiment was prepared[43] by exchange between solid sodium chloride containing ^{22}Na and liquid natural sodium, the two being heated overnight at 250°, after which the sodium was distilled out. When the ratio Na:NaCl $\simeq 10^4:1$, practically complete transference of activity from NaCl to Na was obtained under these conditions.

ACTIVITY COEFFICIENTS IN MIXED SOLUTIONS

The use of radiotracers to determine activity coefficients of minor components in a mixed solution was suggested by Schubert,[42] and this technique has been employed[43] to obtain the activity coefficients at effectively zero concentration of the chlorides of sodium, potassium, rubidium and cæsium in hydrochloric acid solutions, and of sodium chloride in solutions of lithium and potassium chlorides. The distribution of tracer between the solution and Dowex-50 resin in ionic form corresponding to one of the components (e.g. in the hydrogen form for the MCl + HCl system) was first found for a very dilute solution of both electrolytes, and was used to calculate the equilibrium constant for the system $M^+ + \text{H-resin} \rightleftharpoons H^+ + \text{M-resin}$, assuming that under these conditions $\gamma_1/\gamma_2 = 1$ at constant ionic strength. The distribution was then determined under conditions where one component was greatly in excess, e.g. with [HCl] = ·005 - 1·6 molal and [MCl] = 10^{-6} - 10^{-5} molal. From the distribution of M between the solution and the resin, using values of $\gamma_{\pm(HCl)}$ equal to those for pure solutions of HCl at the same concentrations (since the traces of MCl will affect $\gamma_{\pm(HCl)}$ only very slightly), values of $\gamma_{\pm(MCl)}$ at zero concentration were calculated. In this way it was possible to verify Harned's expression[44] for the variation in activity coefficient of the minor component with concentration, viz.:-

$$\log \gamma_2 = \log \gamma_{2(0)} - \alpha_2 m_1 = \log \gamma_{0(2)} + \alpha_2 m_2 \qquad (1)$$

where $\gamma_{2(0)}$ refers to the pure salt solution at the ionic strength employed, $\gamma_{0(2)}$ to the pure salt solution at zero concentration and the same ionic strength, m_2 is the salt molality, and m_1 the acid molality, α_2 being a constant. This expression is complementary to that confirmed earlier by e.m.f. measurements for the activity coefficient of hydrogen chloride as trace component in solutions of alkali chlorides, viz.:-

$$\log \gamma_1 = \log \gamma_{1(0)} - \alpha_1 m_2 = \log \gamma_{0(1)} + \alpha_1 m_1 \qquad (2)$$

where γ is now the HCl activity coefficient and α_1 a constant. In the present work the expression (1) was found to fit satisfactorily the results for sodium and potassium chlorides, but those for rubidium chloride and cæsium chloride show appreciable deviations.

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SECTION C

THE NATURAL RADIOACTIVITY OF THE ALKALI METALS

By G. R. MARTIN

Introduction

Following upon the discovery of the phenomenon of radioactivity, a thorough search was made for similar manifestations in elements other than uranium. Thorium was soon shown to exhibit a similar behaviour, and, amongst the lighter elements, potassium and rubidium also.[1,2] That the comparatively small effects with these two elements should have been detected at all at that time is a tribute to the care with which the search must have been made and, although other naturally radioactive light elements are now known, potassium and rubidium are still much the most significant among them. That the observed activities were indeed associated with these two elements, and not with some heavy-element impurity, was shown by the fact that salts of these elements of differing origins and dates of preparation gave the same activity per gram of the respective element, and also by the absence of any change in specific activity during fractional crystallisation and similar processes.[1,3-10]

Of the other alkali metals, francium (which occurs in nature as a 1% branch of the actinium disintegration series) is dealt with elsewhere (see page 2506); sodium and lithium have no isotopes of half-life long enough to have geological significance; and caesium (investigated rather carefully on account of its position between the naturally radioactive potassium and rubidium on the one side and francium, with no stable isotopes, on the other) has been shown to be quite inactive by means of photographic plate studies, by demonstrating the isotopic normality of neighbouring elements extracted from caesium minerals, and in other ways.[4,11-13]

The radioactivities of potassium and rubidium are of significance from several points of view: potassium especially is widely distributed in nature in both organic and mineral matter, with consequences which will be discussed in detail below. The natural activity of these elements can also provide a quick and convenient method of quantitative analysis under suitable conditions. General accounts have been given of the significance of the radioactivity of potassium and rubidium.[14-16]

The radioactive constants of potassium

(*a*) Mass Assignment.

Only two isotopes of potassium are readily discernible in the mass spectrum of the natural element - those of masses 39 and 41 - and the assignment of the observed β-activity of the element to one or both of these isotopes (or to a third then unknown) occasioned much discussion and speculation.[17-24] By 'ideal distillation' Hevesy[25-27] achieved a partial separation of the potassium isotopes, and a sample with apparent atomic weight 0·005 units greater than normal was found by Biltz and Zeigert[28] to show a specific activity 4% higher, a result which suggested that the isotope of mass 41 was responsible. Later work[29-31] showed that the increase in activity was only about one half of the relative increase in abundance of this isotope, pointing to an assignment to mass 40; furthermore, ^{41}Ca was not found in calcium extracted from potassium minerals.[32,33] Potassium-40 was detected by Nier[34] who estimated its abundance as 1 part in 8600 of the common isotope ^{39}K. Various other estimates of this ratio have been made[35,36] the most recent determinations giving values of 0·00119%[37] and 0·01174%[38-40] for the abundance of ^{40}K in natural potassium. The natural variations in the potassium isotope abundances have been investigated[41,42] but these do not seem to be important. This assignment has been finally confirmed by the examination of the activity of mass-spectrographically separated samples;[43] milligram amounts of ^{40}K have been separated by this method and used for various studies.[44,45]

(*b*) Half-life of Potassium-40.

The half-life of a naturally-occurring primary radioactive material (*i.e.* one which is not being regenerated by the decay of a longer-lived parent substance) is inevitably too long for measurement by a direct study of the decrease in activity of a sample with time. In cases such as this, two techniques are available:

(i) determination of the disintegration constant by measurement of the number of disintegrations occurring in unit time in a sample containing a known number of atoms, or

(ii) the use of indirect information from geological sources to give estimates of the rate of decay.

Both these methods have been used.

The potassium case is complicated by the fact that both the adjacent isobars of ^{40}K, ^{40}A and ^{40}Ca, are stable. Decay to form either product is therefore possible in principle, and, in fact ^{40}K does decay by two alternative routes: by β-particle (negative electron) emission to give ^{40}Ca[46] and by electron capture to give ^{40}A.[47,48] Positron emission, although energetically possible, is not observed,[49-52] a limit of 0·002% of the disintegrations having been set for this mode of decay.[53] Coincidence studies[54] have shown conclusively that the γ-radiation from potassium is associated entirely with the electron-capture mode of decay, so that the decay scheme can be represented:

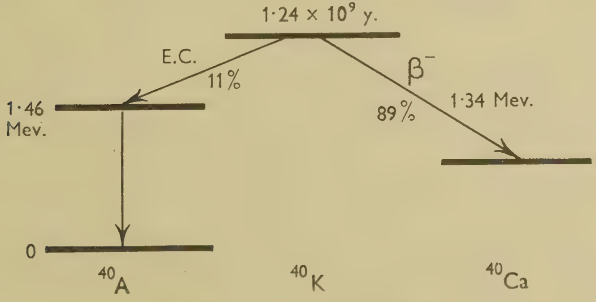

FIG. 1. DECAY SCHEME FOR ^{40}K

The absolute counting of β-particles emitted from a known weight of potassium when combined with the measured abundance of ^{40}K gives a value for λ_β, the disintegration constant for the β-particle emission mode of decay. The specific activity of natural potassium is low (especially in view of the low abundance of ^{40}K) and the measurement is not easy: a 'thin' source gives an activity low compared to the natural background effect of the counter, whilst a 'thick' source involves the rather difficult assessment of the correction for particles absorbed or scattered within the source material. There is now, as can be seen from Table I, substantial agreement on the value to be taken for the specific β-activity of ^{40}K, and it seems reasonable to adopt a value of 29·0 disintegrations per second per g. of natural potassium, corresponding to a disintegration constant λ_β of $5{\cdot}00 \times 10^{-10}$yr^{-1}. (cf. ref. 55).

TABLE I.- SPECIFIC β-ACTIVITY OF NATURAL POTASSIUM

β/sec./g.K.	Year	Authors	Reference	Method
27·1	1950	Houtermans, Haxel and Heintze	56	4π counter
27·1	1951	Good	57	KI (Tl) Scintillator
27·5	1956	McNair, Glover and Wilson	58	Comparison with ^{24}Na
28·3	1950	Sawyer and Wiedenbeck	59,60	4π counter
29·2	1955	Kono	61	KI (Tl) Scintillator
29·6	1955	Suttle and Libby	62,63	K salts counted in screen-wall counter

Other values are given in references 11, 48 and 64-77.

For an estimate of the half-life it is necessary to know also λ_{EC}, since

$$\frac{0{\cdot}693}{t_{0\cdot5}} = \lambda_{total} = \lambda_\beta + \lambda_{EC}$$

This quantity is far more difficult to measure - experimental values of the ratio $\lambda_{EC}/\lambda_\beta$ determined during the past ten years have ranged from 3·0 to 0·02 - and it can, of course, have a profound effect on the calculated value of $t_{0\cdot5}$. The electron-capture process is itself detectable only through the consequent re-arrangement of the extra-nuclear structure of the resulting argon atom, which occurs mainly by the emission of very soft Auger electrons, and measurements of λ_{EC} have mostly been made by indirect means. Coincidence experiments have given results consistent with an electron-capture: gamma ray emission ratio of unity (thus eliminating the possibility that a significant fraction of the electron capture decays proceeds directly to the ground state of ^{40}A, without emission of a γ-ray quantum).[59,78-81] It can thus be assumed that $\lambda_{EC} = \lambda_\gamma$, and the simpler measurement of γ-ray intensity replaces the much more difficult measurement of electron-capture frequency. The alternative approach is to measure the ^{40}A accumulated in a mineral which can be 'dated' by some reliable alternative method. Recent measurements by both techniques seem to group rather closely around a value of λ_{EC} of $6{\cdot}15 \times 10^{-11}$yr.$^{-1}$ (equivalent to a ratio $\lambda_{EC}/\lambda_\beta$ of 0·123), as Table II shows, but earlier values were strikingly discordant.

Combining these two quantities, we find $\lambda_{total} = 5{\cdot}60 \times 10^{-10}$yr.$^{-1}$, corresponding to a half-life of $1{\cdot}24 \times 10^9$ years. At the present time natural potassium is thus producing argon at the rate of $4{\cdot}25 \times 10^{-12}$c.c.STP/g./yr. General discussions of the problems of determination of the half-life of ^{40}K will be found in various review articles.[108-111]

(*c*) Properties of Radiations From ^{40}K.

Although some of the earlier measurements[11,21,66-70,112-117] suggested the presence of two β-ray groups, the absence of β-γ coincidences has now been demonstrated[54] and the simpler decay scheme of Fig. 1 is now known to be an adequate representation. The β-particle energy distribution[57,61,63,118-131] shows an end-point at 1·34MeV., its third-forbidden shape being consistent with a

TABLE II.- THE ELECTRON-CAPTURE BRANCHING RATIO OF ^{40}K

$\lambda_{EC}/\lambda_{\beta}$	Year	Authors	Reference	Method
0·115	1950	Houtermans, Haxel and Heintze	56	γ/β comparison
0·118	1956	Wetherill *et al.*	92	A/K ratio
0·121	1955	Backenstoss and and Goebel	83	γ/β comparison
0·122	1950	Gerling, Titov and Ermolin	84	A/K ratio
0·123	1955	McNair, Glover and Wilson	58,85	γ/β ratio
0·124	1949	Sawyer and Wiedenbeck	60,86	γ/β ratio
0·125	1953	Burch	87	γ/β ratio
0·126	1950	Inghram, Brown, Patterson and Hess	88	A/K; A/Ca ratios
0·127	1948	Graf	89	γ/β ratio
0·13	1951	Sailor, Floyd and Borst	90	X-ray/β ratio
0·13	1954	Wasserburg and Hayden	91	A/K ratio

Other values are quoted in references 47,48,66-68,70-72,74,82 and 93-107.

spin change of 4 units.[57,118,122,132-136] The de-excitation of the ^{40}A nucleus formed by orbital electron capture proceeds by the emission of a single γ-ray quantum of energy 1·46 MeV.[49,50,53,54,58,68,74,121,137-145] with a delay which is probably very short indeed, and is certainly less than 1 second.[52] No evidence has been found for the emission of α-particles from potassium.[11,146] These interpretations are consistent with mass spectrometric values for the masses of the nuclei concerned.[147,148]

Radioactive constants for rubidium

(*a*) Mass Assignment.

It was tempting, by analogy with potassium, to assign the natural radioactivity of rubidium to a hypothetical isotope of very low abundance of mass 86 - intermediate between the known isotopes 85 and 87[17,21,22,24,132,149] - but this has been demonstrated not to be the case. Hahn, Strassmann and Walling[150] and Mattauch[151] examined the isotopic composition of strontium isolated from a rubidium-rich (2–3%) lithium mica from Manitoba, and showed it to be almost pure (99·7%) ^{87}Sr, in contrast to 'normal' strontium which contains only 7·02% of ^{87}Sr. Hemmendinger and Smythe[152] have also shown (by examination of mass-spectrographically separated samples) that ^{87}Rb is the only significantly active isotope of the element. The natural abundance of ^{87}Rb is 27·85%.[153-155]

(*b*) Half-life of ^{87}Rb.

Many determinations of the half-life of ^{87}Rb have been reported, based either on a determination of the absolute specific activity of the element (yielding, with the measured isotopic abundance of ^{87}Rb, a value for the disintegration constant, and thence of the half-life)[8,156-170] or on the examination of ^{87}Rb/^{87}Sr ratios in old minerals which can be dated from other evidence.[171-173] There is now substantial agreement between the two methods, and a value of $5{\cdot}0 \times 10^{10}$yr. for the half-life would seem a reasonable one to take.

The agreement between the two methods (one giving λ_β and the other λ_{total}) would appear to dispose of the suggestion[174-178] that an alternative mode of decay - bound beta-disintegration (the inverse of the well-known electron capture process) - was occurring, undetected in the counting experiments since no particle is emitted, but contributing, of course, to the rate of formation of ^{87}Sr measured in the geological experiments. The measurements of the ^{87}Rb half-life are summarised in Table III. The higher values obtained by the earlier counting experiments almost certainly reflect an inadequate allowance for absorption and scattering of the lower-energy β-particles.

TABLE III.- SELECTED RECENT VALUES FOR THE HALF-LIFE OF ^{87}Rb

Half-life years	Method	Authors	Ref.	Year
$4{\cdot}3 \times 10^{10}$	2π counter	Geese-Bähnisch and Huster	158	1954
$4{\cdot}6 \times 10^{10}$	Geol. (cf. A/K age)	Fritze and Strassman	172	1956
$5{\cdot}0 \times 10^{10}$	Geol. (cf. Pb/U age)	Aldrich, Wetherill, Tilton and Davis	171	1956
$5{\cdot}1 \times 10^{10}$	Cylindrical G.M. counter	Libby	164	1957
$5{\cdot}8 \times 10^{10}$	G.M. counter	Eklund	167	1946
$5{\cdot}9 \times 10^{10}$	RbI scintillator	Lewis	162	1952

Other results are quoted in references 8, 156, 157, 159–161, 163, 165, 166, 168–170.

(*c*) Properties of Radiations from ^{87}Rb.

No γ-radiation is emitted in the decay of ^{87}Rb[158-163] and the decay scheme must therefore be the simple one shown in Fig. 2. Estimates of the maximum beta-particle energy have been made by various workers[7,63,117,132,165,169,179-183] but recent measurements suggest that the maximum energy is 0·275 MeV.[159-163,184]

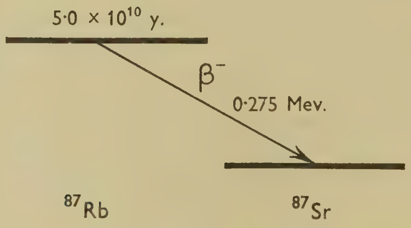

FIG. 2. DECAY SCHEME FOR ^{87}Rb

The distribution in energy of the emitted particles has been measured by means of a proportional counter spectrometer,[161] by a photographic plate technique,[185] by a magnetic lens spectrometer[163] and by means of a thallium-activated rubidium iodide crystal in a scintillation spectrometer.[162] There is substantial agreement about the shape of the energy spectrum, which appears to have a third-forbidden shape.[160,163,181,186] Apparent electron-β-particle coincidences[157,170,179] are now thought to arise from the scattering of β-particles from the source or its support, and not to be indicative of a strongly internally-converted γ-ray.[163,166]

Analytical application of natural radioactivity of potassium

In the absence of other significantly radioactive substances, the natural radioactivity of potassium provides a quick and convenient technique for its determination. The low specific activity of the natural element renders this method unsuitable for very low concentrations but, especially in the region of a few per cent, the method works well. This technique has been applied to process control in the synthetic fertiliser industry, where speed in obtaining the results enables the proportions of feed materials to be adjusted before large quantities of incorrectly balanced product have been produced.

The finely ground sample can be placed in the annular space surrounding a thin-walled Geiger–Müller counter without further treatment, and the observed activity related to that of standards containing known concentrations of potassium. It is implicit in this procedure that standard and unknown samples have the same β-particle stopping power, or that correction has been made for such variations as exist. Correction must also be made for uranium and thorium products present in the phosphate component of fertiliser mixtures.[187–201] Conversely, of course, the γ-radiation from substantial potassium deposits can interfere with prospecting for uranium and thorium minerals by radiological methods.[202]

A large annular counter can also be used, in the absence of other γ-emitters, to determine the total potassium body burden of human subjects.[203–206] The natural radioactivity of potassium has been found inadequate to give good autoradiographs.[207]

Biological significance of the natural radioactivity of potassium

It seems to be well established that plant and animal systems do not significantly change the isotope ratios in potassium.[208–210] Equally, there seems to be no support for the supposition that the radioactivity of the element plays some essential role in the natural function of potassium in biological processes: the concentration of ^{40}K appears, for example, to be without significant effect on the rate of growth of *Aspergillus niger*, which depends rather on the total potassium concentration.[211–214] Potassium does, of course, make its contribution to the natural radiation to which living material is exposed, but there is no reason to think that, even in earlier times when the ^{40}K abundance was greater, it had any pronounced biological effect.

Geothermal significance of natural radioactivity of the alkali metals

The present-day rate of energy release from potassium is 27×10^{-6}g.-cal./g./yr., and from rubidium 36×10^{-6}g.-cal./g./yr.[215,216] The chemical similarity between the two elements ensures that their geological distributions are rather similar and, since the natural abundance of rubidium is so much less than that of potassium (approximately 1/100th)[217] it is permissible virtually to ignore the contribution of rubidium to the radioactive heat production in the earth.

The geothermal history of the earth has, of course, been partly governed by the rate of radioactive energy release during geological time, and this will have been greater in the past than it is at present on account of the exponential decrease with time of the amounts of radioactive substances. The true value of the half-life of ^{40}K is thus of some importance in this connection, and some of the larger values ascribed at one time to λ_{EC} would have led to half-lives so short that the rate of energy release in the past would have been very difficult to reconcile with geological evidence. With the currently accepted value of λ_{EC} (leading to a half-life of $1{\cdot}24 \times 10^9$ years) this difficulty largely disappears.

Geothermal measurements show that the earth is at present losing heat at the rate of about 1·2 × 10^{-6}g.-cal./cm.^{2}/sec. The thermal diffusivity of the earth is thought to be so low that very little of the heat generated below a depth of about 400 miles will have reached the surface by conduction through the solid even in a time of the order of several thousand million years. One can then set an upper limit to the average potassium content of the earth's mantle, in terms of the rate of production of heat (ignoring the contributions from the natural uranium and thorium series) and the observed present rate of loss of heat. A value of 0·37% K is thus obtained[218] but this must certainly be too great, for the integrated heat retention would be some three times greater than the heat of fusion of the rocks of which the mantle is thought to be composed, and fusion would be followed by convective heat transport, which would be considerably more efficient than conduction through the unmelted solid. Assuming a uniform distribution of potassium, an acceptable upper limit would be more like 0·13%; the abundance of potassium in typical crustal rocks is, of course, substantially greater than this (e.g. granite about 3%; basalts about 1%) so that the mantle must be composed of rocks substantially poorer in order to maintain this average value.

The argon of the atmosphere is commonly regarded as being almost entirely of radiogenic origin: its isotopic composition is unusual (cf. the potassium-argon atomic weight anomaly) and its global abundance is out of line with those of the neighbouring noble gases, neon and krypton, which have no radioactive progenitors. A lower limit to the mean potassium content of the mantle can be set by assuming that the whole of the argon produced in it during the past, say, 4 × 10^9 years had escaped into the atmosphere. A minimum of 0·014% potassium would be required to produce this situation; and if some had been retained (as must certainly be the case) a correspondingly higher concentration would have been required.[108]

These values may be compared with the estimates of the average potassium content of stony meteorites, commonly regarded as being typical of the undifferentiated silicate phase of the primitive earth. Older values for potassium in stony meteorites were almost certainly too high, and recent values seem to point to an average of about 0·1%, not at all inconsistent with the foregoing estimate.[219]

The geothermal significance of the radioactivity of potassium has also been discussed elsewhere.[220-226]

The radioactivity of potassium in geochronology

The natural radioactivity of potassium opens up the possibility of 'dating' geological specimens by techniques analogous to the well-known uranium-lead and thorium-lead methods, with the added advantage provided by the ubiquitous nature of potassium.[46,47,67,98,107,108,229-232]

The branched decay of potassium gives two possibilities: measurement of ^{40}K/^{40}Ca and of ^{40}K/^{40}A ratios. The former has been proposed by Ahrens[233] but suffers from the serious limitation that, on account of the high abundance of ^{40}Ca in 'primordial' calcium, the method could only be applied to essentially calcium-free potassium minerals. Such materials are rare, and almost all the experimental work on the dating of potassium-bearing rocks has been done by the examination of potassium/argon ratios. Even in this case, several difficulties arise:

(1) ^{40}A is by far the most abundant isotope in present-day argon,[37] so it is necessary to prevent contamination by atmospheric argon and to eliminate (or allow for) the possible presence of 'primordial' argon in the sample.

(2) Argon can diffuse from some samples at a rate which may be significant on a geological time-scale.

(3) The total disintegration constant for ^{40}K, and the branching ratio for the electron-capture mode of decay must be known accurately: until quite recently this has been a serious limitation.

On the other hand, the extraction and measurement of a small quantity of a gaseous daughter product (argon) is rather easier than the analogous operation with a non-volatile daughter substance (calcium). With the addition of isotopic dilution techniques it has become possible to measure very small quantities of gas, and the potassium/argon technique shows considerable promise in regard to quite recent sedimentary rocks.

It is generally considered essential to check mass-spectrometrically the isotopic purity of the argon extracted, to guard against atmospheric contamination. Argon is usually extracted from samples by vacuum fusion with a well-degassed flux. The gases thus released are purified and the argon measured gas-volumetrically, followed by mass-spectrometric examination for ^{36}A and ^{38}A (indicative of atmospheric contamination, or of the presence of primordial argon). Alternatively a 'spike' of ^{38}A (produced, essentially isotopically pure, by neutron irradiation of sodium chloride, through the sequence

$$^{37}\mathrm{Cl}(n,\gamma)^{38}\mathrm{Cl} \xrightarrow{\beta^-} {}^{38}\mathrm{A})$$

is added before the fusion and the ^{40}A content of the sample deduced from the known amount of ^{38}A added and the mass-spectrometrically measured $^{40}\mathrm{A}/^{38}\mathrm{A}$ ratio; in this case the gas-volumetric measurement of the extracted gas is unnecessary, and, indeed, the only quantitative step essential to the process is the initial mixing of the added 'spike' with the radiogenic argon of the sample. The presence of ^{36}A is taken as indicative of contamination by contemporary or primordial argon. An analogous method based upon the other stable argon isotope (^{36}A) as a tracer has also been used, and the behaviour of these very small quantities of argon in a vacuum system has been checked by means of the radioactive ^{37}A used as a tracer.[234,235]

A technique potentially useful where only very small quantities are available is the neutron activation analysis procedure applied to the argon (through the 109 min. ^{41}A produced by the (n,γ) reaction in ^{40}A). This, of course, provides no check on contamination by contemporary or primordial argon. It is unfortunate that this procedure cannot, in this instance, be applied to the unseparated material: if a potassium bearing material is irradiated with neutrons the reaction $^{41}\mathrm{K}(n,p)^{41}\mathrm{A}$ produces the same product nucleus in quantities likely far to outweigh the product from the radiogenic argon in the specimen.[236,237]

Correction for the presence of non-radiogenic argon must be made with some caution, for two reasons:

(1) The isotopic composition of primordial argon dissolved or otherwise trapped in the solidifying rock is not known with any great accuracy. The ^{40}A abundance in the atmospheric argon of earlier times will have been lower than at present (since more ^{40}A has since been added to the atmospheric reservoir through the decay of potassium); on the other hand, the rock may well have solidified in an environment rich in radiogenic argon, and thus have occluded 'inherited argon' derived from an earlier rock undergoing metamorphosis. It is known, for example, that the $^{40}\mathrm{A}/^{36}\mathrm{A}$ ratio in natural gases from fumaroles and soffioni is higher than in atmospheric argon;[238,239] there is also evidence to suggest that a few minerals (beryl, for example) may be able to occlude quite large amounts of argon in the same way that helium is taken up by them.[240]

(2) There exists the possibility that ^{36}A and/or ^{38}A may have appeared as products of some unsuspected nuclear reaction. Iron meteorites, for example, show a $^{38}\mathrm{A}/^{36}\mathrm{A}$ ratio of 1·7 (compared with the ratio 0·19 in atmospheric argon), these nuclides presumably arising (along with ^{40}A) as products of

spallation reactions induced in iron by cosmic ray particles.[241-243] ^{38}A is also found in uranium and thorium minerals, presumably as the end product of a nuclear reaction either induced directly by alpha-particles, or arising as a secondary product of alpha-particle produced neutrons. An alternative suggestion is that ^{38}A is the decay product of a hitherto-unknown long-lived isomeric state of ^{38}K, since the ^{38}A contents of samples analysed by Gerling *et al.* appeared to be proportional to the potassium content, and to increase in an appropriate manner with the age of the sample; there is at present no confirmation of this suggestion.[244-249] It would thus seem prudent to view with some suspicion any age determinations which have involved substantial corrections for argon not immediately derived from the decay of the ^{40}K content of the specimen.

The question of possible loss of argon from samples by diffusion also needs careful consideration. There is now a substantial body of data obtained from co-genetic pairs of samples, in which dating has been effected by the potassium/argon technique standardised by some alternative method (usually 'concordant' uranium/lead measurements, or rubidium/strontium estimations). It seems not unusual for feldspathic materials to give ages which are fairly consistently about 30% too low; some feldspars, indeed, show a significant rate of loss of argon after crushing preparatory to analysis. On the other hand, micas seem much more satisfactory, giving potassium/argon ages in quite good agreement with those obtained by the uranium/lead or rubidium/strontium methods on co-genetic materials.[91,92,97,104,234,250-265] Much work of a related nature has been done by Gentner and his collaborators, and others, on sedimentary rocks. Potassium is a common constituent of these deposits, and the sensitivity of the method offers considerable promise of an absolute dating technique which could be applied to fossiliferous materials, providing an unequivocal inter-relation between the radioactive dating methods and the conventional geological approach. It is especially important for this purpose to ensure that there is no 'inheritance' of argon from detrital grains incorporated in the sediment, since these would contain argon appropriate to their original date of crystallization rather than to the date of formation of the sediment. Sylvite is an obvious possibility, containing a high concentration of potassium and having crystallized from an aqueous solution which may be presumed to have been in equilibrium with the atmosphere. Unfortunately, the investigations of Gentner and others have shown that argon can diffuse at a significant rate in sylvite - coarser grained material is richer in argon than the finer grained samples of similar age - and a diffusion coefficient $D = (1{\cdot}5 \pm 1) \times 10^{-19}$ cm.^{2}sec.$^{-1}$ has been estimated for argon in this material at 40°C. Glauconite has more recently been proposed as a material suitable for the potassium–argon dating of sedimentary deposits. Glauconite is a potassium-bearing silicate common in sedimentary rocks and it is thought to be formed, in general, within a relatively short time of the formation of the sediment itself. It has a relatively large grain size; being ferruginous, it is easily separated from the remainder of the deposit by magnetic separation of the crushed rock; and its mica-like structure augurs well for its argon retentivity. Provided the necessary geological safeguards are observed, the potassium–argon method has adequate sensitivity for the dating of deposits of only a few million years age.[264,266-272]

The application of this technique is by no means limited to terrestrial materials. Several determinations have been made on samples of stony meteorites, although the potassium content is usually small enough to call for some care in the determination; in particular, the low argon/potassium ratio characteristic of the tektites has been taken as an indication of the comparatively recent origin of these bodies.[106,258,273-279] In addition to the papers cited specifically in the foregoing account, there are many other accounts of experimental techniques and of the results obtained with them; it should, however, be borne in mind that some of this work was carried out before the disintegration constants of potassium were accurately determined, and that the results may need re-calculation in the light of more modern information.[88,94-96,100,163,261,271,278,280-303]

In addition to the procedures outlined above, in which one attempts to 'date' specific geological samples in terms of the argon which has accumulated since the last occasion on which gases could have escaped from the specimen (fixing, in general, the date of solidification from a melt or a solution), various authors have attempted the converse type of calculation. It is clear from the low abundance of all the noble gases relative to the neighbouring elements that the earth's primordial stocks of these elements were largely lost at an early stage in its development. The relatively smaller depletion of argon, and its rather unusual isotopic composition, have led to the assumption that virtually all the argon in the atmosphere is of radiogenic origin, and some conclusions can then be reached about the time needed for its accumulation.

It seems fairly certain that the potassium content of the earth's crust is too low to account for the total argon content of the atmosphere and, if solidification of the crust effectively sealed off the argon being produced in the mantle, it would be necessary to assume that the surface of the earth had remained fluid for at least several hundred million years after escape of argon had effectively ceased. Unfortunately, the total quantity of potassium contributing to the atmosphere-forming process is not at all clearly defined, and such calculations as these can be expected to give values which are at best only plausible. In some cases, the calculations have been based on data now known to be in error. On the assumption that water vapour would have escaped from the primordial earth along with the noble gases, Kulp has shown that the subsequent escape of water from the interior of the earth on a basis analogous to that for argon would provide sufficient to account for the present extent of the hydrosphere.[46,111,219,304-315]

On a more certain basis is the work on the isotopic composition of meteoritic potassium, which has shown that the specific activity of this element extracted from stony meteorites is the same, within experimental error, as that of terrestrial potassium. It follows that potassium from these two sources is all derived from the same 'creation' or, if not, that the two processes were so related as to make the present-day abundances just the same - a most unlikely circumstance.[316-318] Houtermans and Jordan[319] have suggested that the argon/potassium ratio in old minerals might provide a suitable system for a test of the theory of Dirac and Jordan which would call for a systematic variation in the ratio of K-capture to β-emission probabilities with time; it seems unlikely at present that it would be possible to eliminate all other sources of variability with a sufficient degree of certainty to make this a reliable test.

The radioactivity of rubidium in geochronology

Although rubidium is of much less common occurrence than potassium, the dating technique based on the measurement of ^{87}Sr/^{87}Rb ratios shows considerable promise, especially (in view of the long half-life of ^{87}Rb) in relation to the older rocks. As compared with the other methods, the following advantages may be mentioned:

(1) No gases are involved in the decay process, so that loss of daughter products through gaseous diffusion does not occur (cf. the potassium/argon method where the daughter product is itself gaseous, and the methods involving uranium or thorium decay, which depend to a greater or lesser extent

on retention of the radon members of the decay chain).

(2) The commoner rubidium-bearing rocks are not notably rich in primordial strontium, and ^{87}Sr is, in any case, a relatively rare constituent of common strontium (7·02% abundance). Correction for primordial strontium contamination can therefore be made with fair confidence (cf. ^{40}A and ^{40}Ca, which are by far the most abundant isotopes of their respective elements; and the lead isotope ratios which show a disconcerting variability in common lead).

Early measurements based on chemical or spectrographic analyses for rubidium and strontium (without mass-spectrometric examination) were of necessity limited to the few minerals (especially lepidolites) relatively rich in rubidium and low in primordial strontium (absence of calcium is indicative of this), in which it was reasonable to assume that the strontium was preponderantly of radiogenic origin.[320–327] Since about 1950, mass spectrometric techniques have been increasingly applied, with two immediate advantages: the greater sensitivity of the isotopic dilution technique removes the requirement for high rubidium content, and makes it possible to examine minerals (e.g. biotites) of far commoner occurrence; and the measurement of three stable strontium isotopes makes possible a reasonably accurate correction for primordial strontium contamination, so that the technique is no longer limited to minerals essentially free from common strontium. In addition to the stable isotope dilution technique, neutron activation analysis has recently been applied to the estimation of trace quantities of rubidium in rocks; analyses can now be carried out on biotite samples as small as 100 mg.[328–333]

The correction for the presence of primordial ^{87}Sr is commonly made by reference to the ^{88}Sr content of the sample, and therefore rests on the constancy of the ratio ^{87}Sr/^{88}Sr in the primordial element. Variations of up to 5% have been found in the ^{86}Sr/^{88}Sr ratio, and, on general grounds, it would be expected that the variation in the ^{87}Sr/^{88}Sr ratio would be only half as great. In general, the error introduced by this assumption is not thought to be great, although care must obviously be taken if the primordial strontium content is significant compared to the radiogenic material as, unfortunately, tends to be the case with the fairly widely distributed (and therefore potentially most useful) biotites.[334–338]

The rubidium/strontium method shows a tendency to give 'ages' somewhat higher than those obtained by other techniques. This may simply imply that the half-life for ^{87}Rb at present accepted is too long (the abnormally high proportion of low energy β-particles in the ^{87}Rb decay makes absolute counting unusually difficult), or it may be that both the potassium/argon and the lead methods are more subject to diffusion errors so that the higher ages may, in fact, be correct. Another factor which must be borne in mind is that remelting (or re-crystallisation) of a potassium mineral almost certainly involves loss of the accumulated argon, whereas the same is not necessarily true of a similar process with a rubidium-bearing mineral, where some or all of the previously accumulated strontium may well be retained on re-solidification. It should be noted that some of the ages quoted, especially in the earlier literature, may need re-calculation in the light of more recent values of the disintegration constants. In addition to the references quoted above, a number of other publications[253,254,265,276–278,302,303,339–354] give geological ages obtained by this method, and details of experimental techniques employed.

The rubidium/strontium decay can also, in principle, be used in an inverse sense for dating marine sediments. Since the ^{87}Sr/^{88}Sr ratio in common strontium should be increasing as ^{87}Rb decays, a deposit free from rubidium (limestone and anhydrite both contain very little) should show a ^{87}Sr/^{88}Sr ratio characteristic of its date of deposition. Little work along these lines seems yet to have been done.[336,338,354–357]

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SECTION CI

FRANCIUM

By A. G. MADDOCK

The element of atomic number 87, the heaviest of the alkali metals, was named 'francium' by Mlle. M. Perey,[1] who discovered the element in 1939.[2] The name was chosen in honour of France, the discovery having been made in the Curie laboratory of the Institut du Radium in Paris. The pronunciation *frăn sĭ ŭm* was recommended by the Committee on Nomenclature, Spelling and Pronunciation of the American Chemical Society.[3] The name and the symbol Fr were adopted by the International Union of Pure and Applied Chemistry meeting in Amsterdam in September 1949.[4] The commission on Atomic Weights, following its practice for elements not available in macroscopic amounts, decided that the official table should indicate the mass of the most stable known isotope in square brackets, viz. Francium, Fr, [223].[5] The American Chemical Society accepted these decisions in 1951.[6]

Earlier names for the element, based on unsubstantiated claims to the discovery, include russium,[7] alkalinium,[8] virginium[9] and moldavium.[10]

HISTORY

The existence of a sixth alkali metal was already indicated by the earlier forms of the periodic classification of the elements advanced by Mendelejeff. A space was shown for an unknown element tentatively denoted as *ekacæsium.*[11] The prediction of ekacæsium is discussed in the original Treatise[12] but at that date some confusion still existed regarding the assimilation of the rare earths in the periodic classification. This confusion arose because attempts were still being made to incorporate these elements without discontinuity into the body of the earlier form of the periodic table and when this was done two homologues of cæsium were predicted. These difficulties were resolved as it was gradually realized that the atomic number, and not the atomic weight, was the true characteristic of an element. Siegbahn and Friman's[13] studies of the L_α and the L_β *X*-ray spectra of the heaviest elements showed that spaces could be found for elements of atomic number 85, 87 and 91 between tungsten and uranium. The spectra of all the known elements, with the exception of emanation and actinium which they were unable to examine, showed the regular progression predicted by Moseley's law after allowance was made for the above mentioned vacancies. In addition it became clear that only one homologue of cæsium could be found between that element and uranium. Similar conclusions were drawn by Wagner.[14]

Several attempts were made during the first three decades of this century to discover the missing element. The possibility that ekacæsium would prove radioactive was recognized at an early date[15] but a number of investigations were conducted using methods of detection which could only prove successful in the detection of a stable or a very long-lived species. These investigations are conveniently classified according to the method of detection employed.

A very careful comparison of the sensitivities of these methods was made by Bainbridge.[16] Supposing that the atomic weight of the unknown element must be about 223 and that an analytical determination of the atomic weight could distinguish differences in the fifth significant figure in the atomic weight, Bainbridge concluded that gravimetric analysis could succeed only on a concentrate containing 1 part of ekacæsium in 10^4 of cæsium. Bainbridge doubted whether optical spectroscopy would prove much more sensitive, partly because of the contribution to the background from the glare from the spectra of the other alkali metals present and partly because the *raies ultimes* should lie in the infra-red. Dabrosserdow also argued that the sensitivity of spectroscopic methods of detection might be unusually low.[7] The possibility of preferential excitation of the ekacæsium spectrum was, however, acknowledged. Bainbridge concurred with Hevesy[17] in estimating that the excitation of the characteristic *X*-ray spectrum would be about one order of magnitude less sensitive than optical spectroscopy and he showed that mass spectrometric methods should be capable of detecting one part of ekacæsium in 10^7 parts of cæsium. Radioactive methods were not strictly comparable with the above methods and the sensitivity of a reported physiological method of detection of ekacæsium could not be estimated.

Atomic Weight Studies.

The earliest deliberate attempt at the concentration and detection of ekacæsium was made by Richards and Archibald[18] who subjected 150 g. of cæsium dichloriodide to 25 stages of fractional crystallization. The atomic weight of the cæsium separating in the most soluble fraction was compared with that of the initial material. No significant difference was found. A similar, but larger scale, investigation was made by Baxter.[15] 3·5 kg. of cæsium nitrate were separated from a sample of pollucite from Paris, Maine, U.S.A., containing 33% of cæsium, rubidium and potassium and 2% of sodium and lithium. The mineral was extracted with nitric acid and treatment of the residue with hydrofluoric acid showed that a negligible proportion of the alkali metals was retained by the residue. Aluminium and other elements were separated from the nitrate solution by adding ammonium hydroxide and the precipitate was filtered off. The solution was then evaporated and the residue was gently ignited to drive off ammonium salts. 3·5 kg. of cæsium nitrate thus prepared were subjected to fractional crystallization until the least soluble 3 g. were separated. The atomic weight of the cæsium contained in this fraction was not significantly different from the accepted value. This investigation was criticized by Dennis and Wyckoff[19] who pointed out that the solubilities of potassium, rubidium and cæsium nitrates leave some doubt as to the solubility of ekacæsium nitrate.

Optical Spectroscopy.

Richards and Archibald[18] examined the flame spectrum of the product of their attempt to concentrate ekacæsium, but they found no new lines. Baxter[15] also tried spectroscopic methods and investigated the flame and spark spectra of his product without positive results.

A much more extensive study was reported by Dennis and Wyckoff.[19] The alkali metals contained in 3·5 kg. of pollucite were separated by extracting the powdered mineral with concentrated hydrochloric acid for between thirty and forty hours. Other metals were separated by treating the extract with ammonium hydroxide and a slight excess of ammonium carbonate. The precipitate was separated and dissolved in sulphuric acid, and the alums formed were separated by crystallization and returned to the main body of the alkalis in the supernatant solution from the carbonate precipitation. Repetition of the carbonate precipitation and recovery of the alkalis that might be entrained in this precipitate eventually gave a complete recovery of the alkali metals. After conversion to chlorides the mixture was then subjected to systematic fractional crystallization. To avoid the possibility of losing ekacæsium chloride during the crystallizations, evaporations were conducted under reduced pressure. The arc spectra of all the fractions were recorded and examined from the ultra-violet to the infra-red without finding evidence of the missing element. The fractionation was repeated using the perchlorates and the alums formed from the same sample of cæsium. The arc spectra of all fractions were taken in both cases, but without success.

Amongst the most likely terrestrial sources of a missing alkali metal are the salts of the seas. Friend examined a sample of Dead Sea water.[20] The sample had a density of 1·2089 at 18°C. and was taken from a depth of two feet about fifty yards off shore at the northern end of the sea. The most soluble chloride fraction of the salts was separated by fractional crystallization and the alkali metal chloroplatinates precipitated. No lines that could be attributed to a new element could be detected with this precipitate. A few years later it was suggested that the element might become concentrated in the deepest parts of the ocean and so might be found in the water from the Mindano depths.[21]

During the first quarter of this century the spark spectra of a wide variety of alkali metal source materials were investigated by Murmann.[22] Although cæsium was detected, by means of its line at 3861·5 A., in cigar ash, water from the North Sea, commercial magnesium chloride, rubidium alum and potash from beet molasses, no evidence of a new element could be obtained, nor did it appear in cæsium alum or in the mother liquors from the preparation of oxalic acid or lithium salts.

Some attempts were made to facilitate the examination of the spectra of likely materials by calculating the wave-lengths of the principal lines of the ekacæsium spectrum. By making an empirical extrapolation from the data on the spectra of the known alkali metals, Loring[24] estimated that lines would be found in the ekacæsium spectrum at 8015·88, 4830·69, 4175·83, 3906·89, 3766·26, 3682·46 and 3628·15 A. He found that a line in the cæsium spectrum reported by Meissner[23] closely corresponded with the first of these wave-lengths and all the remaining six wave-lengths lay within 1·5 A. of lines found by Sommer[23] in the same spectrum. On this evidence he suggested that ekacæsium was a common impurity in cæsium salts and that it should be called 'alkalinium'.

Corrections and extensions of some of the calculations appeared subsequently,[24] and later it was suggested that ekacæsium might be responsible for the unidentified strong line at 6374·5 A. in the spectrum of the solar corona.[25] An identification of the first doublet in the principal series of ekacæsium in sun spot spectra had already been claimed by Russell.[26] It was argued that the anticipated low boiling point and low first ionization potential would make it likely that ekacæsium, if present in the sun, should be observed in the coronal spectrum.[25,27] Loring's method of calculating the spectrum and first ionization potential of ekacæsium was empirical and imprecise as, indeed, he admitted in later papers where he substantially modified his earlier wave-lengths.[28] Subsequent and more reliable calculations have given quite different values (see below).

It may be remarked that in this series of papers Loring does not comment on his earlier claim to the discovery of ekacæsium using *X*-ray spectroscopic methods of detection, although he had not formally withdrawn this claim (see below).

Bainbridge[16] calculated the separation of the ekacæsium doublets as 1675 cm.$^{-1}$, and showed that no such doublet, having the appropriate frequency and intensity relations, could be found in the solar spectrum between 7000 and 9000 A.

An extensive but unsuccessful search for ekacæsium was made by I. and

W. Noddack.[29] Alkali fractions were separated from pollucite, beryl, samarskite, gadolinite, æschynite and other sources. The cæsium fractions were then fractionally crystallized, using either the alums or the chloroantimonites, and the least soluble fractions thus isolated were examined by emission spectroscopy, particular attention being paid to the region of the infra-red where the *raies ultimes* of ekacæsium were expected to lie.

X-Ray Spectroscopy.

The success of *X*-ray spectroscopy in the unambiguous demonstration of a vacancy for ekacæsium and its apparent specificity as a means of identification stimulated interest in the application of the technique to the search for this element. The first attempts were made by Loring and Druce, the former having already discussed the question of the number and nature of the missing elements.[30] While examining some manganese compounds, primarily with a view to the discovery of elements 43 and 93, they noticed a line in the *X*-ray emission spectrum at 1·032 A. Other plates showed a similar line apparently at 1·040 A. These were interpreted as the unresolved doublet $L\alpha_1$-$L\alpha_2$ of ekacæsium.[31] The nature of the material used, except that it was derived from pyrolusite, and the methods of chemical concentration were never fully disclosed.[32] In the earlier communications no evidence of the $L\beta$ lines could be found, and their absence was attributed to the strong absorptions in this spectral region due to the presence of silver and bromine in the photographic plates. However, on more careful examination a faint line at 0·837 A. was found and this was identified with the $L\beta$ line.[33] Interpolation from Siegbahn and Friman's data[13] indicated that the $L\alpha_1$ line should be found at 1·0276 A.[34] Intensification of the first of these films moved the centre of the $L\alpha$ line nearer to the calculated value and away from the $L\beta_1$ line of mercury which should appear at 1·0458 A. Negative results were obtained when similarly lengthy exposures were made using Kahlbaum's manganous sulphate,[35] the $L\beta$ line remaining very shadowy.

The evidence for the existence of traces of ekacæsium in manganese compounds advanced by Loring and Druce thus depended on the observation of a line in the *X*-ray emission spectrum on three plates, at 1·032 or possibly 1·040 A., attributed to the unresolved $L\alpha_1$–$L\alpha_2$ doublet of the element, and a very doubtful observation of an $L\beta$ line, 0·837 A. It was criticized anonymously by a writer who pointed out that the $L\beta_1$ line of mercury occurs at 1·040 A. and that mercury from the diffusion pump commonly appears in the *X*-ray spectrogram when long exposures are used.[36] Moreover it was observed that the claim to the discovery was based on the attribution of one or possibly two among a number of unidentified lines on the films. Notwithstanding the cogency of this criticism, Loring reaffirmed his belief in his claim in several subsequent publications,[38] one of the strongest arguments justifying his position being the absence of the lines on the control exposure with manganous sulphate.

The difficulties of *X*-ray spectroscopy, in particular the appearance of anomalous lines, misled a number of other investigators who tried to make use of this potentially powerful method for the detection of ekacæsium.[37]

An unsuccessful attempt to apply the same method of detection was reported by Herzfinkiel[39] who mentioned an earlier failure by Dauvillier and Ponte. Similar results were reported by Friend[20] and Noddack,[29] using the concentrates they had examined by optical emission spectroscopy. The *X*-ray emission spectrum of Karlsbad salts was shown to be free from lines due to ekacæsium.[40]

A positive result was reported by Papish and Wainer using the alkali fraction from samarskite.[41] 10 kg. of the ore was treated with hydrogen chloride at 1000° and the volatile chlorides, including the alkali metal chlorides, were converted into sulphates. The other metals were separated by precipitation with ammonium hydroxide and the filtrate was evaporated and the residue was ignited to expel ammonium salts. After solution of the precipitate in hydrochloric acid, the most soluble chlorides were separated by fractional crystallization. The perchlorates were precipitated from this fraction and converted successively into chlorides, sulphates and then alums. The least soluble alum was separated by fractional crystallization. Lines were found in the X-ray emission spectrum at 4·517 (M_{α_1} ?); 1·026 (L_{α_1} ?); 1·038 (L_{α_2} ?); 0·853 (L_{β_2} ?) and 0·944 (L_{η} ?). A Siegbahn X-ray spectrograph was used. Some time later it was shown that some, at least, of these lines arose from imperfections in the crystal and in the spectrograph (see below).

A positive result was also reported by Mlle. Hulubei, who examined the spectrum of a concentrate prepared from pollucite and found lines at 1·032 and 1·043 A. Interference from mercury was avoided by the use of an oil diffusion pump. The preparation of the concentrate was not described, but a sensitivity of one part in 10^7 was claimed. The name 'moldavium' was proposed.[10] Hirsh pointed out that a Moseley plot of Siegbahn's data[13] indicated that the separation of the L_{α_1} and L_{α_2} lines of ekacæsium should not exceed 6 or 7 X. Using a rocking crystal spectrograph containing the crystal used by Papish and Wainer, Hirsh found positive results with a concentrate of cæsium hydrogen sulphate prepared from lepidolite by Kennard, but similar lines were obtained upon blank exposures and were shown to be due to imperfections in the crystal. These lines vanished when the rocking amplitude was increased.[42] Some years later Hirsh confirmed the absence of ekacæsium in this material by showing that L_{α} lines could not be excited as fluorescence by molybdenum K radiation.[43]

Mlle. Hulubei, however, continued to believe in the validity of her results. Using a focussing X-ray spectrograph of the kind designed by Mlle. Cauchois, she found lines corresponding to the L_{α_1} and L_{α_2}, as well as the L_{β_2} line, when either quartz or mica crystals were used in her spectrograph. She pointed out that the latter line was unlikely to be simulated by the lines in the spectra of other elements. Interference by mercury and tungsten was avoided by the use of a tantalum filament and an oil diffusion pump.[44] An attempt was made to concentrate the element by fractional crystallization of the alkali chlorides obtained from 20 kg. of pollucite and the L_{α_1} line was reported to be intensified in the most soluble fraction. Negative results were obtained with alkali chlorides derived from beryl but positive results were reported for autunite and colombite from Bavaria and for pitchblende.[45]

By the time Mlle. Hulubei's last publication appeared it was already clear that no long-lived isotope of this element existed.[46]

Mass Spectrographic Studies.

Bainbridge[16] concluded that mass spectrographic methods should be capable of detecting less than one part of ekacæsium in 10^6 parts of cæsium. He examined the cæsium fraction separated from samples of pollucite and lepidolite from Oxford county, Maine, U.S.A. The ion source was a hot tungsten filament treated with the alkali concentrate and maintained at 1200–1300°K., and a Dempster type mass-spectrograph was used. The results showed that the pollucite contained less than $3{\cdot}5 \times 10^{-7}$ parts and the lepidolite less than $7{\cdot}3 \times 10^{-6}$ parts of ekacæsium.[16] Murawkin[47] found an anomalous line at mass number 222, using a molten glass ion source and a circular mass-spectrograph, but it was shown that this was probably due to a molecular cadmium ion, Cd_2^+. An examination of the concentrate prepared by Papish and Wainer[41] in a Dempster type mass-spectrograph, using an ion source with an oven at 600–700°C., gave an ion beam corresponding to a mass number of 222.[48] Possibly this also was due to a molecular cadmium ion.

Other Non-radioactive Studies.

A supposed indication of the presence of ekacæsium in solutions of cæsium salts has been based on the physiological behaviour of the solutions.[49] An unsuccessful attempt to concentrate the element by differential ionic migration has been made.[50] Equally unsatisfactory results attended an attempt to detect the element by means of the mobility of the ions in a rare gas atmosphere, using a concentrate consisting of the least soluble chloroplatinates formed by the alkalis contained in 2 kg. of Norwegian samarskite.[51] It was estimated that the concentrate contained less than one part of ekacæsium in 4000.

The discovery of ekacæsium in pollucite and lepidolite was one of the first successes claimed for the now discredited magneto-optic method of analysis.[52] Papish and Wainer[41] objected that the effects observed, which were then believed to depend on the masses of the ions in the solution, might be due to the $ReCl^+$ or $SnCl_3^+$ ions. These, however, were shown to produce different minima,[53] and so the discovery of ekacæsium was claimed and the new element was called 'virginium'.[9] Six isotopes, of mass numbers 217, 219, 221, 223, 225 and 227, were reported and these were accommodated in a modified form of $4n + 3$ or actinium decay series and in a new $4n + 1$ series.[54] The method was soon invalidated and its insufficiency for the detection of ekacæsium was conclusively demonstrated by Papish and Shuman.[55]

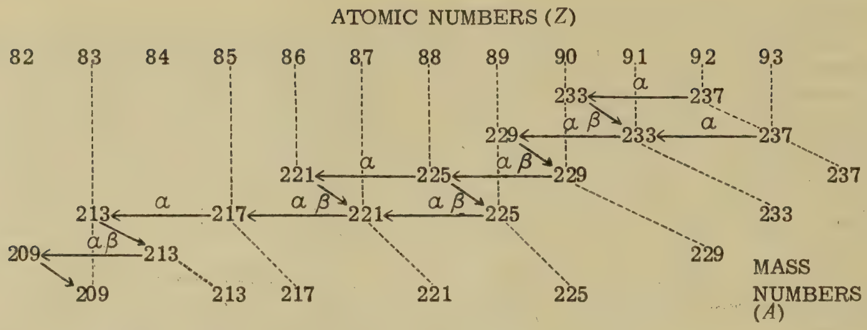
Radiochemical Studies.

Almost as soon as the serious search for ekacæsium began, it was recognized that the element would probably prove to be radioactive. In many cases it was assumed that one isotope at least was sufficiently long-lived compared with the age of the earth to permit its detection in nature, even if it were not continuously replenished by the decay of some parent species.

Ebler examined the water, salts and mother liquor from Rhenish wine by means of an electroscope and found that the alkalis contained therein were weakly radioactive.[56] He attributed this activity to the presence of ekacæsium, but it has been pointed out that he was probably unaware of the activities of potassium and rubidium.[57] Baxter[15] and Friend[20] both examined their concentrates in the hope of detecting ekacæsium by means of its activity. Loring[25] and Kendall[50] suggested that the activities reported for potassium and/or rubidium might, in fact, be due to ekacæsium. An activity attributed to ekacæsium was reported by Aartovaara, who examined samples of alum separated from the alkalis contained in gadolinite and Finnish felspars.[58]

As knowledge of the radioactive decay processes accumulated and the principal features of the three natural decay chains became established, rather more explicit predictions about the nucleogenesis of ekacæsium became possible. Its position in the periodic classification and its odd atomic number made it likely that all its isotopes would be radioactive and might have relatively short half-lives.[36] Speculations appeared regarding the mass number of the most stable isotope and the atomic weight of the element. The first of these predicted an atomic weight of 224, by means of an entirely empirical numerical treatment developed from the data on the lighter elements.[59] Dobrosserdov agreed with this value.[7] As Aston's data on the masses of the isotopes accumulated, it appeared more likely that the most stable isotopes of ekacæsium would possess odd mass numbers. Russell reached the conclusion that the isotope of mass number 221 would be most stable.[60] In a further publication he reported that isotopes of mass numbers 219 and 223, which would be members of the missing $4n + 1$ series of radioactive species, might also occur.[61] The following alternative decay schemes for this series were postulated.

Washburn[62] and Loring[28] found that an atomic weight of 223 was more likely. Reference has already been made to the isotopes purported to have



been discovered by the magneto-optic effect.[54]

Supposing that only short-lived isotopes of the element existed, it was realized that the element must be sought in association with one or other of the natural radioactive decay series. Russell shrewdly suggested that the element might be associated with the undiscovered $4n + 1$ series. It could be formed either by the alpha decay of an isotope of actinium or by the beta decay of an isotope of emanation, but the known isotopes of these two elements had been found to be beta and alpha active respectively. It was possible, however, that one or other of the isotopes showed a subsidiary branch decay process.

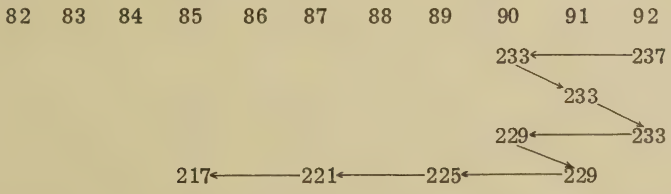
Of the two naturally occurring isotopes of actinium, Hahn found that meso-thorium II did not emit any α particles,[63] whereas actinium was at first believed to be rayless. However, Cranston reported that a weak α activity was associated with meso-thorium II.[64] The question was re-investigated with great care by Hahn. In the first series of experiments he used 57 mg. of a radium-contaminated meso-thorium preparation. Cæsium was added as a carrier and separated, after the addition of hold-back carriers, as the chloroplatinate. The measurement of the activity of the purified cæsium began two days after the beginning of the separation. The very weak activity detected showed the same half-life and radiation characteristics as those of thorium C.[65] He concluded that the branching ratio for α-decay by the meso-thorium II must be less than 10^{-4} if the half-life of the ekacæsium were two hours, or less than 10^{-7}, if the half-life were ten years.[66] In a further investigation, using speedier separation procedures, the maximum branching ratio for α-decay was reduced to $2{\cdot}9 \times 10^{-7}$, supposing the half-life of ekacæsium lay between ten minutes and ten years.[66] A similar investigation was made by Hevesy,[37] who also tried to detect the alpha activity of meso-thorium II directly by scintillation methods. Guében, however, claimed to have detected a weak group of rather short range alpha-particles in a freshly prepared meso-thorium II preparation.[67] The meso-thorium II contained in 2·5 mg. of meso-thorium was separated by the method of Hevesy.[37] 30 mg. of lanthanum nitrate was added as carrier and precipitated by ammonium hydroxide. The lanthanum hydroxide precipitate carrying the meso-thorium II was redissolved in nitric acid and the precipitation was repeated. After again dissolving the precipitate in nitric acid, a small quantity of thorium nitrate solution was added, followed by hydrogen peroxide and ammonium hydroxide until precipitation just occurred. This thorium peroxide precipitate carried down the ionium and radiothorium together with some of the thorium B and C. Barium was then added to the solution and barium sulphate precipitated. The precipitate carried down the radium, thorium X and meso-thorium I remaining in the solution. Finally small amounts of lead and bismuth carriers were added and precipitated with hydrogen sulphide. This precipitate removed the thorium B and C. Each of these stages was repeated three times. The activity of the final meso-thorium II sample was measured in an ionization chamber with a compensated electrometer. The range of the α-particles, measured with a pair of chambers,[68] was 3·03 cm. in air at n.t.p. Such a value would imply a very long half-life for ekacæsium, so that it might be expected to occur in macroscopic amounts in thorium minerals.[69]

The possibility of the formation of ekacæsium by the beta-decay of radon was investigated by Hevesy[37] using 100 mc. of radon. A branching ratio of less than 10^{-6} was obtained. The other isotopes of emanation have not been studied so thoroughly.

The association of a weak alpha-activity with actinium has been known for many years.[70] Hahn and Rothenbach found that about 0·2–0·3% of the disintegrations took place by alpha-decay, and in the following year the range of these alpha-particles was reported to be 3·4 cm. at n.t.p.[71] At a later date, however, it was suggested that these alpha-particles arose from the presence of traces of the parent protactinium in the samples of actinium used.[72]

In addition to these experimental studies, Rona and Schintlmeister plotted the energy surfaces of the atoms in the vicinity of element 87 and came to the conclusion that actinium and meso-thorium II should both prove to be alpha-active, but that the branching ratio for this mode of decay might be too small for experimental detection in the case of the latter isotope. They considered beta-activity of the emanations unlikely.[73]

The artificial production of ekacæsium was first discussed by Walke[76] who suggested that isotopes of the missing $4n + 1$ series might be produced by the neutron bombardment of thorium. He modified Russell and Widdowson's decay scheme as follows:-



Some highly speculative papers on the radioactivity of ekacæsium also appeared. Lepape suggested that the alpha-decay of ekacæsium, following its concentration in plant materials, was responsible for some of the helium in natural gases.[74] The improbability of this hypothesis was emphasized by Szelényi.[75]

The isotopes proposed on the basis of magneto-optic methods of detection were considered by Bishop[54] and Graham.[77] The unsuccessful search for ekacæsium was the subject of a number of reviews.[7,11,29,78-89]

DISCOVERY OF FRANCIUM

Although the alpha-activity of actinium was discovered so many years ago, it was not until January 1939 that the product formed by this mode of decay was identified and the branching confirmed.[2] Mlle. Perey purified a sample of actinium by co-deposition of the radioactinium on ceric hydroxide. The actinium B and C were removed on a lead sulphide precipitate. Finally the actinium was co-deposited on a lanthanum hydroxide precipitate leaving the actinium X in solution. A beta-activity was observed to grow in the purified actinium with a half-life of 21 minutes. The absorption curve of these beta-particles in aluminium gave a coefficient μ of 39 $cm.^{-1}$ The emission of alpha-particles of 3·5 cm. range at n.t.p. by the purified actinium was confirmed. The beta-active substance could be separated on a cæsium carrier, and it was identified as the isotope of element 87 of mass number 223 and called actinium K. This name was obviously applicable only to the one isotope so that the element was subsequently named *Francium.*

PHYSICAL PROPERTIES OF FRANCIUM

Since no long-lived isotopes of this element are known, and it is indeed unlikely that any can exist, the only physical properties directly determined relate to the radioactive properties of the various isotopes. However, a large number of estimates of different properties have been made and these will be considered separately.

Extrapolated or Theoretical Properties.

Atomic Radius.

The radius of the atom has been estimated as 3·7 A.[90]

Atomic Volume.

Various estimates, based on extrapolation of the data for the alkali metals have been made. Dobrosserdow[7] gave 98 cm^3/g. atom; Graham[77] 80·5 cm^3/g. atom at 20°C. Hicks[91] and Yagoda have also discussed this property.

The Diatomic Fr_2 Molecule.

By means of empirical relations between the atomic weight of an element and the characteristic frequency of its diatomic molecules, Matsuyama[93] and Clarke[94] have estimated the frequency for the Fr_2 molecule to be 30·1 cm^{-1} Another estimate,[95] depending upon regularities in the potential energy curves for such molecules, indicated a value between 22 and 27 cm^{-1}

Recently Varshni has estimated the frequency by means of the relation, $\log W = g - h \log n^2V$, where V is the first ionization potential, n the quantum number of the valency shell and g and h are constants calculated from the data for the other alkali metals.[111]

Boiling Point.

Loring suggested 615°C.,[25] but in a later paper considered 863°C. possible.[27] Graham[77] suggested 620°C.

Melting Point.

Dobrosserdow[7] gave 17·8°C., Loring[25] 15°C., Graham[77] 23°C. and Korff[97] 18°C.

Specific Heat.

Graham[77] gave 0·02 and Loring[98] 0·0338 g.-cal./g./°C., both by a similar graphical extrapolation from the data for the other alkali metals.

Density.

Dobrosserdow[7] obtained 2·3–2·4 and Graham[77] 2·2 g./c.c., by calculation from their estimates of the atomic volume. Loring[99] calculated a value of 2·1.

Ionic Radius of Fr^+.

Ahrens[100] estimated a radius of 1·80 A. for Fr^+ by extrapolation.

The entropy[101] and specific viscosity[102] of the francium ion have been estimated by similar calculations. In addition the structures of the francium halides[103] and of the free metal[104] have been discussed. A few other properties of the metal, including the work function, 1·5 volts,[105] and the specific resistivity,[99] 45×10^{-6} ohm. cm. at 18°C., have been considered. It has also been predicted that the metal would show photoelectric activity at relatively long wave-lengths.[77]

Relatively little weight can be given to the above estimates of the physical properties of the element and its compounds, nor is it likely, in the absence of moderately long-lived isotopes, that experimental values of these quantities will become available within the next few years.

Optical Properties and First Ionization Potential.

The first ionization potential and the spectrum of francium are more amenable to precise calculation and several fairly concordant estimates have been made. Two methods of calculation have been employed. Bainbridge[16] used the known spectrum of the isoelectronic Ra$^+$ ion. Yagoda[106] used an empirical relation between the quantum defect and the principal quantum number of the valence electrons of the element: subsequently he reported[92,107] modified values based on a more direct calculation. For the principal series the following wave-lengths (A.) were obtained:-

$7^2P_{1/2}$	$7^2P_{3/2}$	$8^2P_{1/2}$	$8^2P_{3/2}$	
8720	7600	–	–	Bainbridge[16]
8130	7460	4310	4260	Yagoda[106]
8104	7150	4328	4225	Yagoda[92,107]

Thus, the spectrum should consist of a widely spaced doublet in the red and a closer doublet in the violet. These data differ from the values obtained by Loring[99] by direct extrapolation from the alkali metal spectra. The spectrum has also been discussed by Meggers.[108] A number of estimates of the first ionization potential have been made. Values deduced by extrapolation include 4·24 V.;[109] 4·05 V.;[16] 3·57 or 3·519 V.[24] and 4·11 V.[92] Another estimate was 3·83 V.[111] More recent and elaborate calculations[110] gave 4·0 ± 0·1 V. for the first and 21·5 V. for the second ionization potential.

RADIOACTIVE PROPERTIES OF THE FRANCIUM ISOTOPES

In addition to the naturally occurring actinium *K*, ^{223}Fr, ten other isotopes have been reported.

Francium-223.

The principal radioactive characteristics of ^{223}Fr, determined by Mlle. Perey[112] and her collaborators, have been collected in a review.[113] More recently the photon radiation associated with the decay of ^{223}Fr has been studied in greater detail.[114–118] The half-life of ^{223}Fr is 21 ± 1 minute.[112,113] ^{223}Fr is formed in 1·2% of the disintegrations of ^{227}Ac. The maximum energy of the beta-particles is 1·20 MeV.; the mean energy 265 KeV.; and the most probable energy 150 KeV.[112,113]

Photon Emission.

Earlier suggestions of a hard γ-radiation proved incorrect.[112,113] Mlle. Perey reported photons of 95 KeV. Other emissions at 15·6 and 36 KeV. were attributed to actinium or its decay products. Rion,[115] however, found a photon emission at 38 KeV. Hyde[118] has carried out a very detailed analysis and finds photons of 49·8 KeV. in 40% of the disintegrations and of 80 KeV. in 24% of the disintegrations, as well as infrequent emission at 215 and 310 KeV. *L X*-radiation was also observed.[118] Although beta-decay is the predominant mode for ^{223}Fr, it has been predicted that detectable alpha-branching should occur.[73,119] This has now been observed with a branching ratio of 4 × 10^{-5}, and gives rise to a naturally occurring isotope of astatine.

Francium-221.

The second isotope of francium to be discovered confirmed the earlier predictions that the principal decay route of the $4n + 1$ series of radioactive elements would involve elements 85 and 87.[76] ^{221}Fr was identified during the 1939–45 war as a decay product of ^{233}U. The latter nucleus decays by alpha emission to produce ^{229}Th, which in turn gives ^{225}Ra. This isotope is beta-active and gives ^{225}Ac, which forms ^{221}Fr by alpha-particle emission.[121,122] The half-life of ^{221}Fr is 4·8 min.[123] and it emits alpha-particles of 6·30 MeV. (75%) and 6·05 MeV. (25%).[124,125]

Francium-222 has been made by the proton bombardment of thorium. Its half-life is 14·8 minutes. It decays principally by beta-emission, the maximum beta-particle energy being 2·04 MeV.; but between 0·01 and 0·1% of the disintegrations lead to the emission of 6·00 MeV. alpha-particles.

Francium-220, -219, -218 and -217 have been identified in the decay chains[127,128] descending from ^{228}U, ^{227}Pa, ^{226}Pa and ^{229}U respectively. ^{220}Fr has a half-life of 27·5 sec. and emits alpha-particles of 6·69 MeV.[127] ^{219}Fr has a half-life of 0·02 sec. and emits alpha-particles of 7·30 MeV.[129] Francium-218 has an estimated half-life (Geiger–Nuttall) of 0·005 sec.,[129] and emits alpha-particles of 7·85 MeV. ^{217}Fr has been described by Keyes; it emits alpha-particles of 8·3 MeV.[130]

A closed cycle calculation shows that ^{224}Fr must be unstable to beta-decay by 3·04 MeV.,[130] so that it might be supposed that no other isotopes of half-life more than a few seconds, at most, could exist. However, an abrupt change in nuclear properties occurs in the heavy elements on crossing neutron number 128 and between this value and 125 the alpha-disintegration energy decreases with decreasing mass number. Unexpectedly stable nuclei appear near neutron number 125 and such species have been found for francium.

Francium-212.

Among the proton spallation products of thorium a francium isotope has been discovered having a half-life of 19·0 minutes.[131] It disintegrates by alpha-decay (56%) and orbital electron capture. The alpha-spectrum shows 6·409 MeV., 37%; 6·387 MeV., 39%; 6·339 MeV., 24%.[132]

Francium-211 may also have a half-life longer than five minutes[133] and there is some evidence that ^{210}Fr and ^{213}Fr may have half-lives near one minute.[134]

The systematics of alpha-decay in relation to francium isotopes have been discussed by Berthelot,[135] Biswas,[136] Glass[137] and Momyer.[134] Martin mentions ^{212}Fr as an exception to his relation between the period and $\frac{3}{4}(A-Z)$ for alpha-emitters.[138]

The isotopes of francium have been reviewed by Spitsyn[139] and Hyde.[130]

CHEMICAL PROPERTIES OF FRANCIUM

It is not to be expected that much information could have been obtained about an alkali metal which can be handled only in tracer amounts. Virtually all the chemical data refer directly or indirectly to the separation of francium. The earliest method of preparing actinium K separated the radioactinium from the parent actinium by co-deposition on a ceric hydroxide precipitate formed in the solution by hydrolysis. The species constituting the active deposit were separated on lead sulphide, and the actinium and actinium X were separated on a barium carbonate–lanthanum carbonate precipitate.[140] An alternative method left the actinium K in solution, after precipitating lanthanum fluoride in the solution of the parent actinium. Scavenging by a ferric hydroxide precipitate was necessary to remove traces of actinium X. The products of both these separations are, however, contaminated with Ac C$''$, another beta-emitter, of 4·76 min. half-life.[140,141] The decay curve for such material is shown in Fig. 1.

Separation from the actinium C$''$, an isotope of thallium, is effected by adding a thallous carrier and precipitating thallous chromate or sulphide, or by precipitating potassium tartrate in the solution. The product then displays a pure 21 min. half-life (see Fig. 1). The separation of actinium K, ^{223}Fr, from actinium has been carried out in two operations. Barium, lanthanum and thallium carriers were added to the actinium solution. The first two were precipitated by adding a slight excess of sodium carbonate and the last by adding potassium chromate solution. The actinium K in the remaining solution is then concentrated by adding a cæsium carrier and co-precipitating the

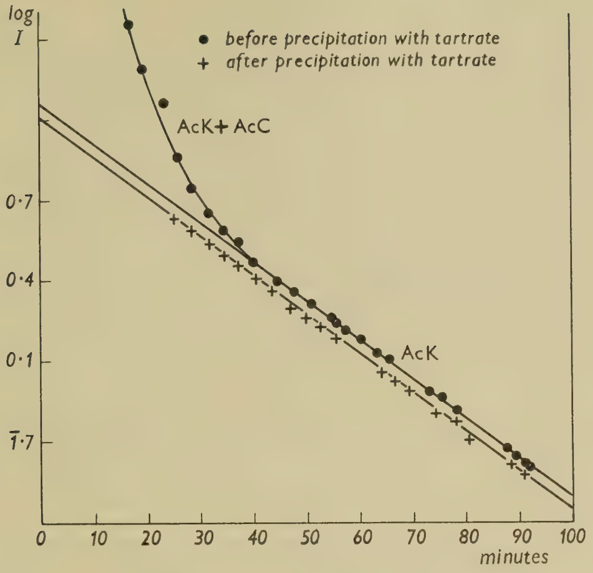


FIG. 1. DECAY CURVE FOR ACTINIUM K + ACTINIUM C″ BEFORE AND AFTER PRECIPITATION WITH POTASSIUM TARTRATE

actinium K on cæsium perchlorate. Naturally it is not possible to produce weightless samples if cæsium is used as carrier. Some attention has been given to the separation of francium from spallation targets of the decay elements. Cæsium was added to the solution as carrier and the francium co-precipitated on cæsium perchlorate in alcoholic solution. The perchlorate was ignited to the chloride, dissolved in water and scavenged by a ferric hydroxide precipitation; then cæsium silicotungstate was precipitated in 6N hydrochloric acid solution, carrying with it the francium. This last operation effects a considerable separation from rubidium isotopes.

Hyde has shown how the above procedure can be modified to give weightless products. The ice-cold solution of the target was saturated with hydrogen chloride and any precipitate removed and discarded. Three or four drops of 0·4 M-silicotungstic acid solution were then added, and the precipitate was washed with cold concentrated hydrochloric acid and dissolved in water. This solution was run onto a 10 mm. × 4 mm. Dowex 50 column (250-300 mesh) and washed through at the rate of 0·5 ml./min. The column was washed with a little water and the francium eluted with concentrated hydrochloric acid. The separation took less than half an hour and the radiochemical purity of the product exceeded 95%, the principal contaminant being cæsium activities. The rubidium/cæsium ratio is reduced to one three hundredth of its initial value. As an alternative procedure the silicotungstic acid can be separated by ether extraction. The separation of francium by paper chromatography has been described,[144] and it is reported that francium and thallium may be separated in this way.[145]

Co-precipitation Reactions.

1. Perchlorate. Perey reports that 60% of the actinium K present co-precipitated on a cæsium perchlorate precipitate.[140]
2. Picrates. 50% co-precipitation on cæsium picrate was observed.[140]
3. Tartrates. Potassium tartrate precipitated in acetic acid solution does not remove francium from the solution, and this may serve as a method of

separation from potassium.[140] Co-precipitation on the more soluble cæsium tartrate has been observed.[140]

4. Platinichlorides. Nearly complete co-precipitation of francium occurs on cæsium platinichloride, but Ac C'' is also carried down.[140]

5. Chlorobismuthite. Nearly complete co-precipitation of francium occurs on cæsium chlorobismuthite, Ac C'' being also carried down.[14]

6. Chloroantimonite. Nearly 90% co-precipitation occurs on cæsium chloroantimonite, with considerable separation from rubidium.[140]

7. Cobaltinitrite. Sodium cæsium cobaltinitrite carries down most of the francium from acetic acid solutions.[140]

Fractional crystallization of francium-containing cæsium alum concentrates the francium in the less soluble portions. The half-life of actinium K, the most stable known isotope, was too short for detailed studies.[140]

The separation of francium on silicotungstic acid precipitates has been described above.[143]

Geochemical Aspects.

Asimov has calculated that the earth's crust contains 24·5 g. of francium.[147] Cody has speculated on the contribution of francium to the radioactivity of the soil.[148] The element has been considered in connexion with the distribution of the isotopes in nature.[149]

Biochemical and Pharmacological Aspects.

Perey and Chevallier have studied the distribution of francium injected into rats. Concentrations in the kidneys, salivary glands, liver, lacteal glands and muscles were less than in other parts of the body. The concentration in a methylcholanthrene tumor in the thigh of one of the rats was found to be twice the average value.[150] Francium and ^{134}Cs were found to concentrate in a benzpyrene tumor whereas ^{86}Rb did not.

Several reviews dealing with francium have appeared.[152-163]

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SECTION CII

THE EFFECTS OF IONIZING RADIATION ON THE SALTS OF THE ALKALI METALS

By H. G. HEAL

HISTORY

Early in the century it was noticed that cathode rays discolour and partly decompose some of the halides and oxyacid salts of the alkali metals. These observations were not followed up until some twenty years later, when the effects of ionizing radiation on the alkali halides began to be intensively studied. This work still continues actively, and though a great deal is known about these effects and their causes many puzzling problems remain. The study of radiation effects in salts containing polyatomic anions was taken up seriously about ten years ago, and is now a lively and promising field, though not far advanced. About the same time, the need for better methods of preparing radioisotopes stimulated an interest in the chemical effects accompanying nuclear transformations in solid salts. This interesting, if rather heterogeneous, field continues to account for a small but steady stream of publication.

GENERAL DESCRIPTION AND CLASSIFICATION OF EFFECTS

When they pass through an ionic crystal, nuclear particles, *X*-rays and γ rays can give rise to any or all of the following effects:-

(i) Ionization and electronic excitation of the atoms of the crystal. This is the main effect of fast charged particles (*i.e.* electrons with energy exceeding a few hundred eV.; α-particles, protons and deuterons with energies of a few hundred thousand eV. or over), and also of *X*- and γ-radiation, the energy of which is communicated to electrons in the act of absorption.[135]

(ii) Displacement of atoms from their normal lattice positions by elastic collisions in which part of the kinetic energy of the bombarding particle is communicated to the atom. If the energy so communicated is small (less than, very roughly, 25 eV.) the result of such a collision is merely to stimulate lattice vibrations that quickly die away. If it is greater than about 25 eV., the atom is likely to be forced out of its normal position into an interstitial position, creating a vacancy.[49,121,230,234]

(iii) Nuclear reactions. These are especially important in bombardments with thermal neutrons, which do not themselves give rise to effects (i) and (ii). However, a nuclear reaction is generally accompanied by a recoil of the disintegrating atom, which may break chemical bonds or cause permanent atomic displacements.[145,283]

Much of this Section (see pages 2523–2560) is concerned with the consequences of electronic excitation and ionization, while a smaller part (see pages 2560–2566) deals with the chemical effects of nuclear transformations. In the present stage of development of the subject it is not necessary to take account of displacements of atoms by elastic collision separately, except in the special case of lithium fluoride (see page 2560), where a nuclear reaction is involved.

Seitz, in a theoretical analysis, has shown that the effects of ionization and excitation must, as a rule, greatly predominate over those of elastic collisions in an ionic crystal.[230,234]

Hitherto, nearly all irradiations have been performed with X-rays, γ-rays, electrons of many thousands of volts energy, or heavily charged particles with energy of the order of 1 MeV. or greater. These radiations expend only about 0·1% of their energy in elastic collisions, and the remainder in electronic excitation and ionization.[230,234] Heavy particles with considerably lower energy would expend a much larger fraction of their energy in elastic collisions; such particles have, however, been used very little in experimental work, because their low penetrating power makes it impossible to affect more than a thin surface film of the crystal. If the effects of elastic collisions were distinctive and characteristic, there might, nevertheless, be some hope of detecting them. Actually, however, at least one of the expected consequences of elastic collisions, viz. the formation of vacancies, also follows upon electronic excitation and ionization.[229,233,234] It is quite likely also that interstitial atoms are formed by way of an ionization mechanism.[271,272] The yield of lattice defects from the ionization and excitation processes is large and the few defects produced by elastic collisions cannot be separately recognized. In fact, except in the special case of lithium fluoride, (see page 2560) no one has hitherto observed any radiation effect in an alkali metal salt which can with confidence be ascribed to atomic displacements by elastic collision.[245]

Bombardment by fast neutrons is rather different.[230,234] Fast neutrons expend a large fraction of their energy in producing atomic displacements, and the effects of these displacements upon the structure and physical properties of metals and semiconductors have been extensively investigated.[49,50,79] But scarcely any information has been published on the effects of fast neutrons in solid salts. One reason for this is that it is not easy to obtain a strong flux of fast neutrons free from other radiations (mainly γ-rays); and after irradiations, e.g. in an atomic reactor, where both types of radiation are present, the effects of the other radiations would usually overshadow those of the neutrons. This problem does not arise with metals and semiconductors, for the effects of electronic excitation and ionization in these are transient and cease when irradiation ends, leaving only the atomic displacement effects, which can then be easily detected.[49,50,79]

To summarize the present situation: no experimental data exist upon which a discussion of atomic displacements by elastic collision in the salts of the alkali metals can be based, except for lithium fluoride. Apart from the discussion of lithium fluoride (see page 2560), elastic collision effects will therefore be disregarded, though it must be pointed out that studies of the action of fast neutrons on the alkali halides are in progress, and will probably give some information on elastic collision effects before long.[34,178]

ELECTRONIC EXCITATION AND IONIZATION

The electronic energy levels of the solid salts of the alkali metals consist of the ground levels; certain narrow bands of excited levels in which the electrons remain bound to their parent atoms, called 'exciton bands'; and, above these, a series of closely spaced levels called the 'conduction band', in which the electrons are not bound to particular atoms, and can move freely through the crystal,[228,233] conferring electrical conductivity. The existence of this system of levels is proved by the nature of the ultra-violet absorption spectra of the salts, in conjunction with their photoconductive behaviour: but there is no individual case in which we have any detailed knowledge of their arrangement. Fig. 1 shows the absorption spectra of a selection of potassium

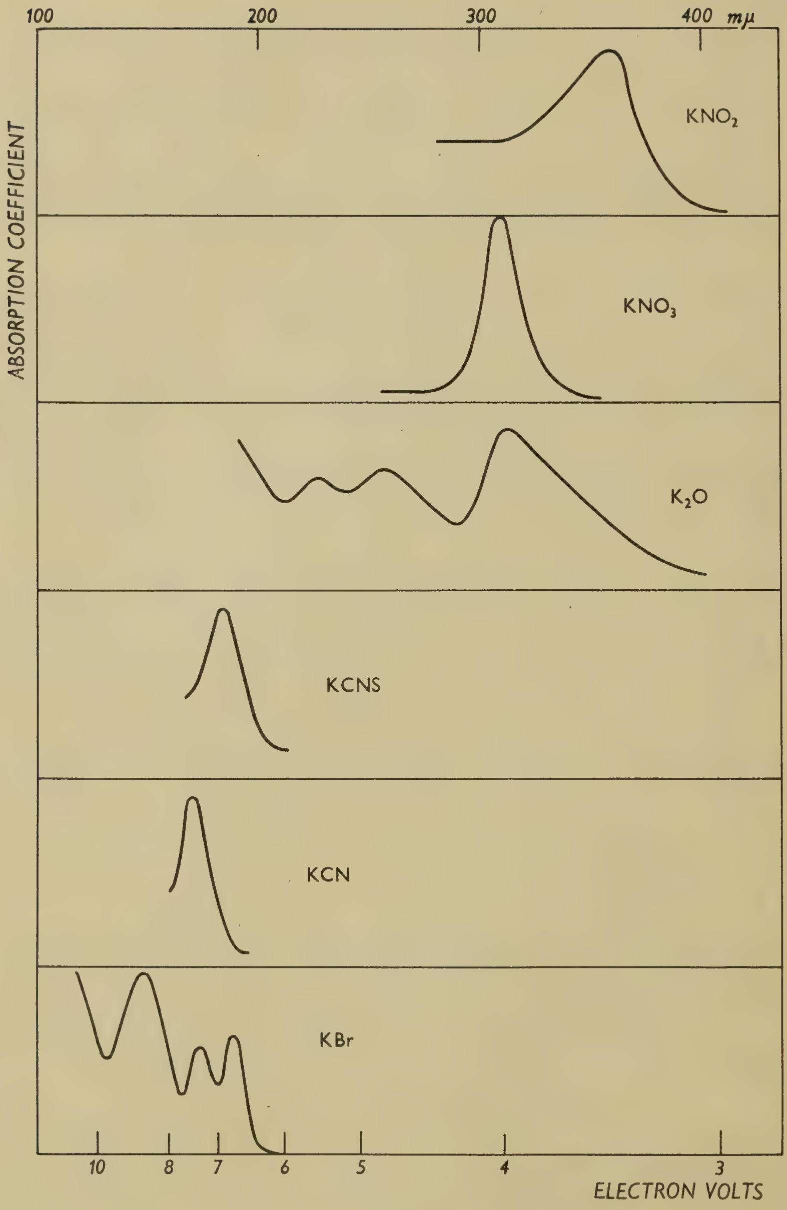


FIG. 1. LONG WAVE-LENGTH END OF THE FUNDAMENTAL ABSORPTION SPECTRA OF A SELECTION OF POTASSIUM SALTS.
THE RIGHT-HAND ABSORPTION BAND IN EACH CASE IS PROBABLY AN EXCITON BAND

salts.[193,209,215,217] In every case the spectrum begins, on the long wave-length side, with one or more separate bands. The first of these are believed to arise from excitation to 'bound' or 'exciton' levels. This has been proved for the alkali halides and potassium azide by showing that light absorbed in the first band does not give rise to photoconductivity;[65,115,233] and it is accepted as the only likely explanation of the first peak in the alkali nitrates and other salts.[209,215] Since the alkali halides become electronic conductors under the action of *X*-rays, there must be an ionization continuum at shorter wave-lengths than the first absorption band.[96,97] There is no precise experimental evidence as to where this begins, but theoretical work indicates that in the alkali halides it probably commences about 1 eV. from the first absorption peak.[233] Thus, some of the peaks shown in Fig. 1 probably lie in the ionization continuum.

Ionizing radiation raises electrons to all these excited levels at once. Even transitions which are optically 'forbidden' take place, with fair probability, by the action of secondary electrons in the energy range 20–100 eV. or so.[134] The immediate products of irradiation are therefore electrons in the conduction band, positive holes (*i.e.* places from which an electron is missing), and excitons of all possible kinds.

All these entities are known to be able to migrate away from the places where they are generated. The relative mobilities of the electrons and holes in sodium chloride have been estimated in the following experiment.[285] A thin sodium chloride crystal was clamped between a pair of electrodes, which were used to maintain an electric field of 175,900 volts per cm. in the crystal. Alpha particles were directed into the crystal through the electrodes. Current pulses were observed only when the alpha particles entered through the cathode, *i.e.* only electron pulses were detected. This result does not rule out the possibility of some hole mobility, since the apparatus was working near the limit of sensitivity with a high noise background, but it is considered to show that the hole range was not more than about one fifth of the electron range.[233] There is independent evidence, e.g. from the bleaching of V_1 centres (**see page** 2547) that holes released from traps in the crystal can travel at least a few atomic diameters.

The motion of an exciton is most easily visualized as the successive transfer of the excitation along a series of neighbouring similar atoms.[69,70,173,228] There is now much indirect experimental evidence that excitons move, though, in the nature of the case, direct experimental proof of their migration can hardly be expected.[233] Seitz has estimated theoretically that excitons in an alkali halide may live as long as 10^{-8} second before emitting their energy as light, and that in this time they could move through about 10^7 ions, spending about 10^{-15} second on each.[233] Since no strong luminescence is observed when the alkali halides are irradiated with light in their first fundamental absorption band (an exciton band), the energy of excitons must usually be degraded into thermal vibration rather than radiated.[233] An exciton travelling through 10^7 ions has almost unit probability of encountering and being trapped at a lattice imperfection;[233] consequently most excitons probably move until they are trapped, and then dissipate their energy in a burst of lattice vibrations at the trapping centre, unless this energy is used otherwise, e.g. in the formation of *F* centres (**see page** 2549) or the breaking of covalent bonds (see **page** 2555). Most of the experimental evidence on exciton migration in ionic crystals relates to alkali halides, but there can be little doubt that excitons migrate easily in the other salts. The ultra-violet photolysis of solid potassium azide has been shown to be a reaction between pairs of excitons which have migrated to lattice defects, and have there been trapped.[115]

The trapping of electrons, holes and excitons at lattice imperfections is fundamental to the explanation of many of the observed effects of radiation in ionic crystals. Empty lattice sites and dislocation lines in ionic crystals have net electric charges associated with them. Impurity atoms and interstitials may be charged, and in any case distort the lattice. Thus, most of these imperfections create potential wells which can function as traps for either electrons or positive holes, according to the sign of the charge on the trap. Neutral traps can also capture electrons in some circumstances (see under F' centres, **page 2544**). The fate of electrons excited into the conduction band by ionizing radiation is as follows. If they have considerable kinetic energy, they lose this to some extent by excitation of atoms, and to a large extent by elastic collisions with atoms, until it has fallen to a value comparable with the potential energy of trapping. They may then encounter and unite with holes (often forming excitons), or be trapped at suitable lattice imperfections. Those holes which are not annihilated by electrons will also wander until trapped.

A question that has been much discussed, and is still more or less open, is whether electrons and holes may become 'self trapped'.[173,229,233] Self trapping might conceivably occur in the following way. If an electron or hole came almost to rest, the ions around it would move to new equilibrium positions in the electric field of the electron or hole and could so create an irregularity in the electrostatic potential of the lattice which might be capable of holding the electron or hole. Actually there is no clear experimental evidence for self trapping, and calculations indicate that it is unlikely to occur under ordinary conditions in the alkali halides.[57,233]

An exciton can be treated as a coupled electron–hole pair,[228] and on this view it is easy to see how excitons can be trapped at the same centres as electrons and holes.

COLOUR CENTRES IN THE ALKALI HALIDES

When exposed to any kind of ionizing radiation, the alkali halides become visibly coloured. In prolonged irradiations the colour may become so dark that the crystals are practically opaque, unless very thin. The visible coloration, and the absorption in the near ultra-violet and near infra-red which the irradiated crystals also display, has been proved to be caused by light-absorbing units consisting of trapped electrons and holes, and of small aggregates of these, known as colour centres.

Most of our knowledge of colour centres comes from studies of their absorption spectra, photoconductivity and optical and thermal transformations. In order to present concisely this large body of information, much of it rather controversial and still under active investigation, the phenomena are here described in general terms and without very much discussion of specific cases. Detailed information is provided in Tables I, II and III (see pages 2528–2535) which give fairly complete references to the sources giving experimental methods, actual plots of absorption spectra and other numerical information, and information on particular substances. These Tables also summarize the principal facts about the constitution, formation and transformations of the centres. Tables IV to VII (see pages 2536–2537) give the peak wave-lengths of the colour centre absorption bands, so far as these are known, derived, wherever possible, from recent original reports or compilations.

Two recent reviews afford much fuller information and discussion on many subjects which can only be touched upon here.[229,233]

The optical absorption bands generated by irradiation of the alkali halides fall into three classes, electron bands, lattice bands, and hole bands.

Electron Bands.

These originate from the absorption of light in centres containing trapped electrons. One of them, the F band, was the first colour centre band to be

TABLE I.- ELECTRON BANDS IN THE ALKALI HALIDES

TABLE 1. - ELECTRON BANDS IN THE ALKALI HALIDES

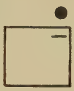
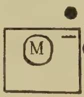
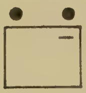
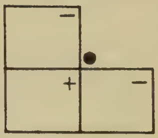
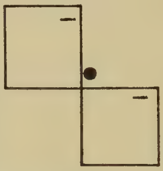
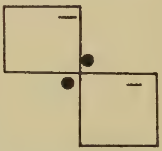
Designation of Band	Substances in which Studied	Probable Nature of Absorbing Centre	Methods of Formation
F (Pohl)	All the alkali halides except LiBr, LiI, RbF, CsBr, CsI. For *F* band in LiF, see Refs. *23,45,46, 86,125-127,149,200, 201* Mixed alkali halides *80,129,164* Alkali halides with hydride additions *2 107,155,156,158,196* Alkali halides with divalent impurity ions *26,27,30,101, 189,190,231*	 (de Boer *42*) perhaps also  (Varley *271*) For symbols see page 2532.	By heating crystal to ∼600°C. in vapour of alkali metal and quenching to room temperature *89,123,148,153,187,196* Irradiation with UV. in tail of fundamental absorption band *5-7,219, 239,242* Irradiation with α-particles *204* Irradiation with protons *138,139,244* Irradiation with β-particles *14,15,56,269* Irradiation with high energy electrons *272* Irradiation with cathode rays *7,9,146,185,204,235, 239,260* Irradiation with *X*-rays at room temperature *28,53, 96,148,158,194,201,218* Irradiation with *X*-rays at low temperatures *28,44, 46,53,58,59,96,125,148, 153,155,200* Irradiation with pile radiation *23* At cathode in electrolysis of crystals at high temperatures *90,122,173* Kinetics of formation *2, 14,15,56,59,96,136,137, 149,151,194,203,218,269* Occurrence in natural rock salt *204,239*
K(Seitz *233*) (V_0)(*L*)	KCl *53,58,59,123, 153,183* KBr *53,58,59,148, 153* RbCl *164*	Absorption probably due to transition to higher discrete levels of *F* centre (Mott and Gurney *173*)	As for *F* band. Observed in crystals coloured by excess metal *74,123* *X*-Rays *28,53,58,59,153* Protons *244*
F' (Pohl)	LiF *23,45* NaCl *188,194* KCl *52,60,96,153, 188,191,196* KBr *52,59,60,148, 188,191*	 (Seitz *229*)	Action of *F* light on *F* centres at temperatures:- below 25°C. in NaCl *188, 194* below –68°C. in KCl *153, 188,191,196* below –130°C. in KBr *59, 188* Direct action of *X*-rays:- below 27°C. in NaCl *194* at –195°C. in KCl *96,153* at or below –183°C. in KBr *59* Formed in slow neutron irradiation of LiF *23*

TABLE 1.- ELECTRON BANDS IN THE ALKALI HALIDES

Thermal Transformations and Stability	Optical Transformations	Photoconductivity and Hall Effect
In crystals containing excess metal, F centres are in equilibrium with colloidal particles in the temperature range ~300°C.-500°C.; they do not bleach at any temperature *167, 184,221-226* In X-rayed crystals, F band bleaches completely on heating to 200-250°C. *59,96, 149,167,171,201,218* If X-rayed at liquid air temperature, bleaches partly on warming to room temperature *28,29,53,156* If X-rayed at liquid H_2 or He temperature, bleaches partly on standing at this temperature by 'tunnelling' *103,152-154*	In crystals containing excess metal, F light converts F band to R_1, R_2, M and N bands at room temperature *187,223* and below room temperature, to F' and α bands *52,153,188* In X-rayed crystals, F light causes some bleaching and some transformation to M, R_1, R_2 and N bands at room temperature *1,2,21,28,82,103, 149,152,171,182* and to F' band at low temperature *21, 171*	Show photoconductivity falling with temperature down to -200°C. *6,7,59, 76,77,106,179-182, 196,210,270* Quantum efficiency for freeing electrons up to 1, dropping with temperature Hall coefficient has sign characteristic of electrons *206*
Probably as for F band, but no specific studies on K band recorded		Photoconductivity observed. K is the only electron-excess band giving strong photoconductivity at -185°C., apart from F' band *180-182*
Reverts completely and rapidly to F centres ($F' \rightarrow 2F$) above:- 25°C. in NaCl *188,194* -68°C. in KCl *60,188* -130°C. in KBr *60,188* but stable at room temperature in LiF *80*	Reverts to F centres ($F' \rightarrow 2F$) when irradiated with F' light *59,148,152,191,196*	Shows photoconductivity under F' light even at very low temperatures *52,88,196* Quantum efficiency for freeing electrons = 1 at all temperatures

Designation of Band	Substances in which Studied	Probable Nature of Absorbing Centre	Methods of Formation
M(Seitz *229*) (*C*)(Petroff *187*)	LiF *23,45,46,125, 126,149,200,201* LiCl NaF *171,183* NaCl *29,149,194, 204* KCl *29,122,139,171, 223,225* KBr *29,181* RbBr *171*	 (Seitz *229*)	Sometimes observed in crystals coloured by excess metal without further treatment *221,223*; enhanced by irradiation of these with *F* light at first *187*; but later diminishes *187* Present in *X*-rayed crystals *29,171,194*; enhanced by irradiation of these with *F* light *171, 229* In crystals irradiated with cathode rays *204* In crystals irradiated with *α*-particles *204* In crystals irradiated with protons *139* In crystals irradiated with slow neutrons (LiF) *23* Formed by electrolysis
R_1(Seitz *229*) (*E*)(Petroff *187*)	LiF *23,46,125,200, 201,262* NaCl *194,204,262* KCl *29,74,139,171, 221,262* KBr *181* RbBr *171*	 (Seitz *229*)	Not formed by *X*-irradiation alone Develops in *X*-rayed crystals or crystals containing excess metal when these are irradiated with *F* light at room temperature *21,29,74,171,194, 221,229*
R_2(Seitz *229*) (*D*)(Petroff *187*)	LiF *23,45,46,183, 201,216,262* LiCl *183* NaF *183* NaCl *29,194,204, 262* KF *171* KCl *29,139,171,221, 262* KBr *29,181* RbBr *171*	 (Seitz *229*)	As for R_1 band
R' (Scott *et al.* *224*)	KCl *224*	Probably a combination of *R* and *M* and possibly other bands (Seitz *233*)	Action of light and heat together, at temperatures below 100°C., on KCl containing excess metal *224*
N (Burstein and Oberley*21,22*) (*G*)(Petroff *187*)	NaCl *21,29* KCl *29,187,221,223* KBr *21,29,181*	No definite evidence See Ref. *233* for suggestions	In crystals containing excess metal *21,187*, or in *X*-rayed crystals *29*, by irradiation of *F* band with *F* light at room temperature Formed weakly by *X*-irradiation alone at liquid air temperature *21,22,29*

Thermal Transformations and Stability	Optical Transformations	Photoconductivity and Hall Effect
In crystals containing excess metal, exists in equilibrium with F centres at temperatures ~600°C. *221, 223, 225* In X-rayed crystals, bleaches completely at 200–250°C.	M light converts it partly to F centres and partly to R centres and N centres *13* M centres with particular orientations selectively bleached by polarized M light *267*	Shows photoconductivity with quantum efficiency for freeing electrons ~0·1 at room temperature Response declines with falling temperature *13, 180-182*
Probably not stable at temperatures much above room temperature in crystals containing excess metal, since it is not formed in conversion of $F \rightarrow$ colloid at ~300°C. *233* In X-rayed crystals, bleaches completely at 200–250°C.	Long believed not to bleach under irradiation with R_1 light *229*, but recent work casts doubt upon this *29, 194, 262*	Photoconductivity declining with temperature reported *179, 180-182*
As for R_1 band	As for R_1 band	As for R_1 band
As for R bands	Bleached by N light *187*	As for R bands

Designation of Band	Substances in which Studied	Probable Nature of Absorbing Centre	Methods of Formation
Colloidal	LiF *201* NaCl *204,214,224, 239* KCl *223,224,255* KBr *224* KI *224*	Particles of alkali metal of colloidal size, visible in the ultramicroscope	Formed in crystals containing excess metal when these are heated in the temperature range 250–500°C. *214,221-226,239, 255* Present in some specimens of rock salt *204,214, 239* Not easily formed in irradiated crystals, since they bleach at too low a temperature. But observed in pile-irradiated *276* and in strongly *X*-irradiated LiF after thermal annealing *201* In electron-bombarded alkali halides *144*

Symbols:- ☐− ☐+ negative-ion vacancy; ● trapped electron; o trapped hole; positive-ion vacancy

TABLE II. - LATTICE BANDS IN THE ALKALI HALIDES

Designation of Band	Substances in which Studied	Probable Nature of Absorbing Centre	Methods of Formation
α (Delbecq, Pringsheim and Yuster *43,44*) (U')	NaBr *155,157* KCl KBr *44,58, 152,155,157* KI *43,149, 155,157* RbBr RbI Alkali halides with hydride additions (See page 2548, for refs.)	Absorption due to optical excitation of halide ion next to a halogen-ion vacancy *233*	Formed in crystals containing excess metal, or in *X*-rayed crystals, when *F* centres are converted to F' centres by *F* light at low temperatures *43,44, 149,152,155* Direct action of *X*-rays at low temperatures *43,44,149,155,157* In crystals containing hydride impurity, by irradiating U band with *U* light below −100°C. (See page 2548, for refs.) By irradiation of KI crystals with light in first fundamental band at −135°C. or lower *47* In spectrum of highly disordered KI (evaporated layers) at low temperatures *149*
β (Delbecq, Pringsheim and Yuster *43,44*)	KCl *122* KBr *44,58, 152,155,157* KI *43,149, 155,157* RbBr *155,157* RbI *155,157*	Absorption due to optical excitation of halide ion next to an *F* centre *233* but alternative structure ☐− has been proposed (Glasner & Tompkins *78*)	Present together with, and proportional in size to, the *F* band in crystals containing excess metal *43,155,157*; also in *X*-irradiated crystals *43,155,157*

Symbols:- ☐− ☐+ negative-ion vacancy; ● trapped electron; o trapped hole; positive-ion vacancy;

Thermal Transformations and Stability	Optical Transformations	Photoconductivity and Hall Effect
Above 600°C. almost completely converted to *F* centres. At lower temperatures in thermal equilibrium with *F* centres; equilibrium favours increasing colloid concentration as temperature falls *223,224,255*	No observations	Weak photoresponse resembling electron emission from metal surfaces *77,179,224*

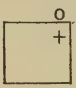
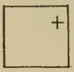
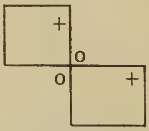
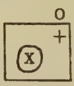
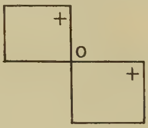
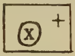
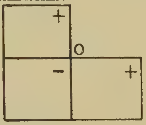
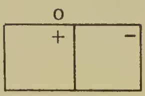
Ⓜ alkali metal atom; ⓧ halogen atom; italic figures are reference numbers.

TABLE II.- LATTICE BANDS IN THE ALKALI HALIDES

Thermal Transformations and Stability	Optical Transformations	Photoconductivity
Disappears on heating above temperature of stability of *F′* centres *233*	Bleached with low quantum efficiency by α light at −183°C. *155-157* In hydride-containing crystals, this bleaching is accompanied by some generation of *U* centres	
Presumably follows behaviour of *F* band	Diminishes proportionately to *F* band when this is bleached by *F* light *155,157*	No direct examination of photoconductivity recorded: but irradiation in β-band causes strong surface photoelectric emission from RbI and KI *8,252,253*

Ⓜ alkali metal atom; ⓧ halogen atom; italic figures are reference numbers.

TABLE III. - HOLE BANDS IN THE ALKALI HALIDES

Designation of Band	Substances in which Studied	Probable Nature of Absorbing Centre	Methods of Formation
V_1	NaCl *29,58* KCl *22,29,53, 59-61,153,254* KBr *22,29,53, 59,60,152, 153,155,156* Mixed alkali halides *192*	 (Seitz *233*) interstitial halogen atom (Varley *271*)  (Glasner and Tompkins *78*)	By X-irradiation at temperatures ~-180°C. *29,53,59-61,152,153, 155,254* (not formed at ordinary temperatures or at temperatures below -250°C.) Alternatively, by X-irradiation below -250°C., followed by warming to ~-180°C. *152,153, 155*
V_2	NaCl *1,29,54, 58* NaI *265* KCl *1,29,53, 54,59,60,153* KBr *1,22,29, 53,54,59,155, 156,158,170* KI *22,54,169, 170,263,265* Mixed alkali halides *192*	 (Seitz *233*)  (Varley *271*)	Heating bromides or iodides in the vapour of the halogen *169, 170* (This method fails with chlorides *233*) Action of X-rays at room temperature or below (most effective at about -40°C. in KCl) *1,53,54,58-60,153,155,158* By electron bombardment *29* Formed at the anode in electrolysis of crystals *263-265*
V_3	NaCl *29,54, 58* NaI *265* KCl *29,53,54* KBr *22,29,53, 54,60,170* KI *22,54,169, 170,263,265* Mixed alkali halides *192*	 (Seitz *233*)  (Varley *271*)	Heating bromides or iodides in vapour of halogen *169,170* (This method fails with chlorides *233*) Action of X-rays at temperatures down to about -130°C. *1,29,53, 54,58,60* By electron bombardment *29* Formed at the anode in electrolysis of crystals *263-265*
V_4	KCl *53,60* KBr *53,59,60, 152,153,155, 156* Mixed halides *192*	 (Seitz *233*) interstitial metal ion (Varley *271*)	Action of X-rays at temperatures below room temperature *53,59, 60,152,153,155*
H (Seitz *233*)	NaCl *58* KCl *58,254* KBr *58,152, 153*	 (Seitz *233*) Hole trapped at interstitial halogen atom (Varley *271*)	Action of X-rays at -268°C. *58, 152,153,254* (Not formed at liquid air temperature or above) By action of V_1 light on V_1 band at -253°C. *254*

Symbols:- negative-ion vacancy; positive-ion vacancy; ● trapped electron; o trapped hole;

TABLE III. - HOLE BANDS IN THE ALKALI HALIDES

Thermal Transformations and Stability	Optical Transformations	Photoconductivity
Bleaches above −145°C. in KCl, *29,60,61,224* and above −158°C. in KBr *60,224*	Bleached by V_1 light at −185°C., with quantum yield only 0·05 *29,60,254* Converted to *H* band by V_1 light at −253°C. *153*	Photoconductivity not clearly demonstrated; quantum efficiency for freeing holes has been estimated as ~0·01, and is certainly much lower than in the other *V* bands *254*
Stable at room temperature in *X*-rayed or additively coloured crystals *29* In *X*-rayed crystals, bleaches rapidly at 150°C. *29*	In *X*-rayed crystals, readily bleached by electrons released from *F* centres by *F* light *233* Bleached by *V* light but recovers on standing in the dark	Relatively strong temperature-dependent photoconductivity *254*
The most stable *V* band; bleaches slowly even at 150°C. in *X*-rayed crystals *29*	In *X*-rayed crystals, not easily bleached by electrons released from *F* centres by *F* light *233* Bleached by *V* light but recovers on standing in dark *1*	As for V_2
Bleaches above −78°C. in KCl *60* and above −27°C. in KBr *60*	No information	As for V_2
Bleaches rapidly at liquid air temperature *58,254*	Bleached by *H* light at −253°C. *254* Diminishes when *F* centres bleached by *F* light at −268°C. *152*	No photoconductivity *254*

Ⓜ alkali metal atom; Ⓧ halogen atom; italic figures are reference numbers.

TABLE IV.- ELECTRON BANDS IN THE ALKALI HALIDES PEAK WAVE-LENGTHS(a) IN MILLIMICRONS

	F		*F'*(i)		*R*$_1$		*R*$_2$		*M*		*N*	
	+20°C.	-186°C.	+20°C.	-180°C.	+20°C.	-180°C.	+20°C.	-180°C.	+20°C.	-180°C.	+20°C.	-193°C.
LiF	250	-	620(e)	-	-	-	310	-	444	-	-	-
LiCl	385	-	-	-	-	-	580	-	650	-	-	-
NaF	340	-	-	-	-	-	415	-	505	-	-	-
NaCl	465	455	-	~510(f)	-	545	-	596	723(d)	713	-	-
NaBr	540	-	-	-	-	-	-	-	-	-	-	-
NaI	588	-	-	-	-	-	-	-	-	-	-	-
KF	455	-	-	-	-	-	570	-	-	-	-	-
KCl	563	548	-	700- 750(g)	674(d)	658	734(d)	727	824(d)	805	1015	980(j)
KBr	630	609	-	700(h)	-	735	-	790	-	892	1090(j)	-
KI	685	662(b)	-	-	-	-	-	-	-	-	-	-
RbCl	624	603(c)	-	-	-	-	-	-	-	-	-	-
RbBr	720	-	-	-	-	805	-	859	-	957	-	-
RbI	775	-	-	-	-	-	-	-	-	-	-	-
CsCl	620(k)	-	-	-	-	-	-	-	-	-	-	-

Notes:-
(*a*) All values come from ref. *247*, except the following:-
(*b*) Value interpolated from ref. *247*
(*c*) Value extrapolated from ref. *247*
(*d*) Values from ref. *213*
(*e*) Value from ref. *45* (Temperature not stated)
(*f*) Value from ref. *188*
(*g*) Value from refs. *52, 153, 191, 196*
(*h*) Value from ref. *58* (Temperature -103°C.)
(*i*) The position of the *F'* peak is badly defined and is uncertain to the extent of about 50 mμ.
(*j*) Ref. *58*
(*k*) Rough value quoted in ref. *113*

TABLE V. - LATTICE BANDS IN THE ALKALI HALIDES PEAK WAVE-LENGTHS IN MILLIMICRONS

(All values calculated from data in ref. 247)

	α (−183°C.)	β (−183°C.)
NaBr	199	–
KBr	202	193
KI	238	226
RbBr	205	197
RbI	240	230

TABLE VI. - HOLE BANDS IN THE ALKALI HALIDES PEAK WAVE-LENGTHS IN MILLIMICRONS

	V_1	V_2		V_3		V_4	H
	−180°C.	+20°C.	−180°C.	+20°C.	−180°C.	−180°C.	−268°C.
NaCl	$345^{(a)}$	$223^{(a)}$	–	$210^{(a)}$	–	–	$330^{(d)}$
KCl	356	$232^{(a)}$	230	$216^{(a)}$	212	~254	$345^{(d)}$
KBr	410	$265^{(a)}$	265	$232^{(a)}$	231	275	$380^{(c)(d)}$
KI	–	$350^{(b)}$	–	$275^{(b)}$	–	–	–

Notes:-
(*a*) Ref. *29*
(*b*) Refs. *169, 170*
(*c*) Ref. *153*
(*d*) Ref. *58*
All other values come from Ref. *247*

TABLE VII. - WAVE-LENGTHS OF BAND PEAKS IN ALKALI HALIDES CONTAINING HYDRIDE AND DIVALENT CATION ADDITIVES (MILLIMICRONS)

	$U^{(a)}$		Z_1 at −215°C. additive:			Z_2 at −215°C. additive:			Z_3 at −215°C. additive:
	+20°C.	−183°C.	Ca^{++}	Sr^{++}	Ba^{++}	Ca^{++}	Sr^{++}	Ba^{++}	Sr^{++}
NaCl	192	–	–	$505^{(c)}$	–	–	$512^{(d)}$	–	–
NaBr	210	–	–	–	–	–	–	–	–
KCl	214	212	$590^{(b)}$	$595^{(b)}$	$600^{(b)}$	$610^{(b)}$	$635^{(b)}$	$650^{(b)}$	$470\text{-}500^{(b)}$
KBr	228	225	–	–	–	–	–	–	–
KI	244	–	–	–	–	–	–	–	–
RbCl	229	226	–	–	–	–	–	–	–
RbBr	242	–	–	–	–	–	–	–	–

Notes:-
(*a*) All values from ref. *247*
(*b*) Ref. *189*
(*c*) Ref. *190*, temperature −203°C.
(*d*) Ref. *190*, temperature −207°C.

discovered, and is nearly always by far the most prominent band in the spectrum of an irradiated alkali halide. Since it usually lies in, or extends into, the visible spectrum, it is generally responsible for most of the visible colouration. In Figs. 2 to 7, illustrating various groups of bands, the *F* band is shown in every figure to serve as a point of orientation.

The evidence that the *F* band is due to trapped electrons is overwhelming: it can be summarized as follows:-

Besides irradiation, there are other methods of generating *F* centres which

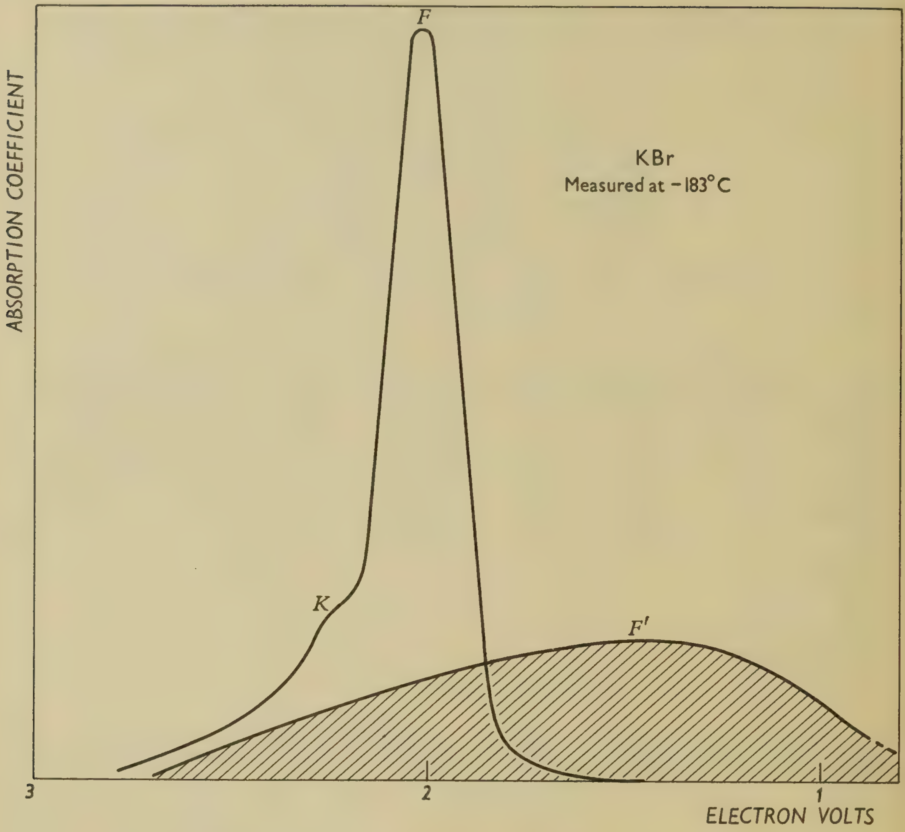


Fig. 2. THE F BAND IN POTASSIUM BROMIDE COLOURED BY EXCESS METAL, AND THE F' BAND OBTAINED BY BLEACHING THE F BAND WITH F LIGHT BELOW −130°C.

give a strong clue to their nature. One such is 'additive colouration', also described as the incorporation of 'excess alkali metal' into the crystal. To achieve this, the crystal is heated in the vapour of an alkali metal at 600–700°C., and cooled suddenly to room temperature. Sudden cooling is needed to prevent the formation of colloidal metal in the intermediate range of temperature (**see page 2545**). The wave-length of the F band developed in this way is identical with that of the F band formed by irradiation, and it is the same whatever the alkali metal used. This shows that the band is due not to metal atoms, but to electrons that are supplied by the metal and diffuse into the crystal, while an equal number of ions of the metal deposit on the surface of the crystal.

A third method of generating F centres is by electrolysis of the crystal at temperatures not far below its melting point. A cloud of F centres appears round the cathode, from which it is reasonable to suppose that electrons enter the crystal. The boundary of the cloud moves towards the anode as electrolysis continues: this is interpreted as the migration of electrons from trap to

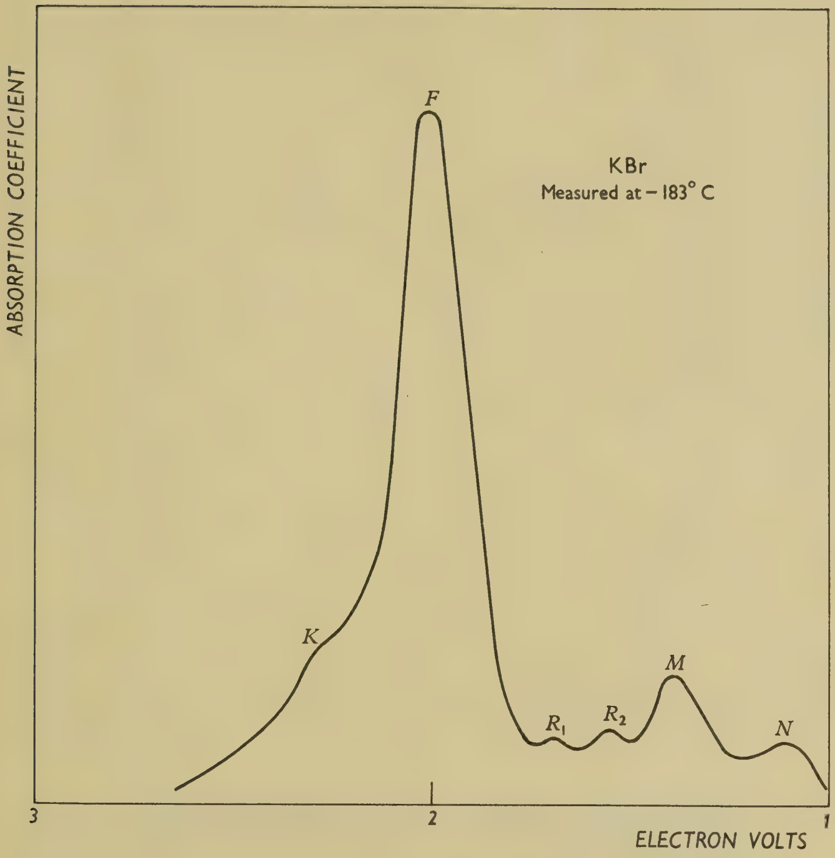


Fig. 3. ABSORPTION SPECTRUM OF POTASSIUM BROMIDE COLOURED WITH EXCESS METAL, AND PARTLY BLEACHED WITH *F* LIGHT AT ROOM TEMPERATURE, SHOWING DEVELOPMENT OF THE *R* BANDS AND THE *M* AND *N* BANDS

trap.[173] (At high temperatures, they are often released from the traps by thermal energy).

Further evidence that the trapped charges are electrons comes from the Hall Effect: crystals containing *F* centres, when illuminated with light in the *F* band, become photoconducting, and have a Hall e.m.f. with polarity corresponding to negative current carriers.[205,206]

In 1937 de Boer suggested that the traps at which electrons are captured to form *F* centres are negative-ion vacancies.[42] This suggestion has been generally accepted, for the following reasons:-

Since the *F* band forms more easily than any other, the traps are more likely to be simple units than complex aggregates. The simplest conceivable mode of trapping is, of course, self-trapping, but this is unlikely on theoretical

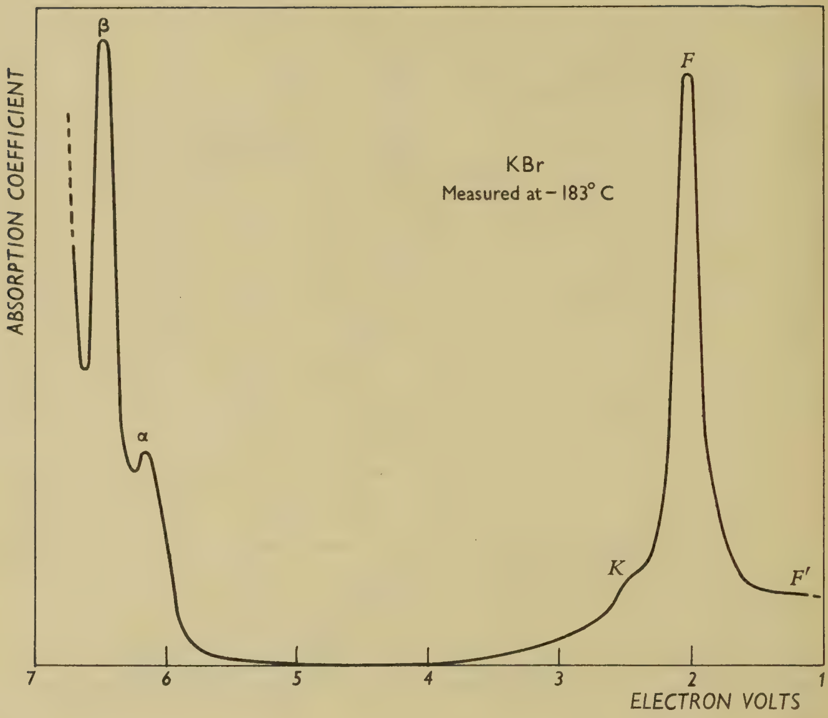


Fig. 4. ABSORPTION SPECTRUM OF POTASSIUM BROMIDE COLOURED BY EXCESS METAL, SHOWING THE α AND β BANDS. THE α BAND HAS BEEN PARTIALLY DEVELOPED BY PARTIAL BLEACHING OF THE F BAND WITH F LIGHT

grounds, and it would be in conflict with the known facts about the equilibrium between F centres and metal vapour.[229] Electron traps could not be negatively charged; they might be either neutral or positive. The traps from which F centres form cannot be neutral, for if they were, the F centre would be negative, and could not capture any further electrons, while F centres do, in fact, capture extra electrons to form F' centres as described below. The traps must therefore be positive. The simplest positive trapping centres are negative-ion vacancies and interstitial positive ions. Both these imperfections must be assumed to exist in ordinary alkali halide crystals; but detailed calculations have shown that in sodium chloride, for instance, the energy required to form an interstitial positive ion and associated vacancy (Frenkel defect) is about 2·9 e.V., whereas the energy required to form a pair of vacancies of opposite sign (Schottly defect) is only about 1·86 e.V.[172] This means that the concentration of interstitial ions in thermal equilibrium must be very much lower than the concentration of vacancies. F centres form easily in well-annealed crystals, in which there must be far fewer interstitial ions than vacancies. Consequently the traps are most probably negative-ion vacancies. There is much corroborative evidence for this view, such as the formation of F centres from U centres (see page 2548), the behaviour of the α

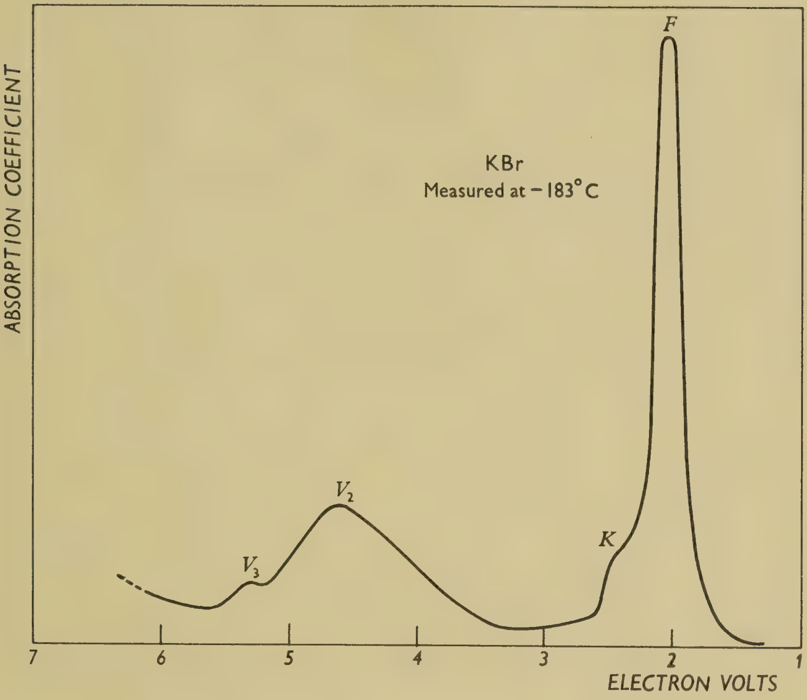


Fig. 5. ABSORPTION SPECTRUM OF POTASSIUM BROMIDE IRRADIATED WITH X-RAYS AT ROOM TEMPERATURE, SHOWING THE V_2 AND V_3 BANDS

band (see page 2548) the expansion of the crystal during X-ray coloration (see page 2549) etc. There are, however, unexplained variations in the half-width of the F band, exceeding estimated experimental errors.[58,271] These have led some investigators to suggest that the band is composite, *i.e.* caused by absorption in more than one kind of centre.[181,271] For instance, some of the centres might consist of a neutral metal atom held in a halogen-ion vacancy, with a trapped electron.[271]

The absorption spectrum of the F centre is entirely consistent with the model just described. A halogen-ion vacancy in an alkali halide crystal can be regarded, as a rather crude approximation, as a charge of $+e$ in a uniform dielectric medium: its potential field is nearly spherically symmetrical. Thus, the F centre possesses a system of energy levels resembling that of the hydrogen atom. The lowest energy state is a *1s* state, and the F band arises from transitions from this state to the *2p* state, which are optically 'allowed' (see Fig. 8).[173] This is the only optical transition taking place with high probability in the F centre.[173] The conduction band begins only a little way above the *2p* level (see Fig. 8), but direct optical transitions from the ground state into the conduction band occur only with low probability.[173] The F band has a noticeable 'tail' on the short wave-length side (see Fig. 2): this may arise from such transitions.[173] There is also a 'shoulder' on the short wave-length side of the F band, called the K (formerly V_0) band, which is not always

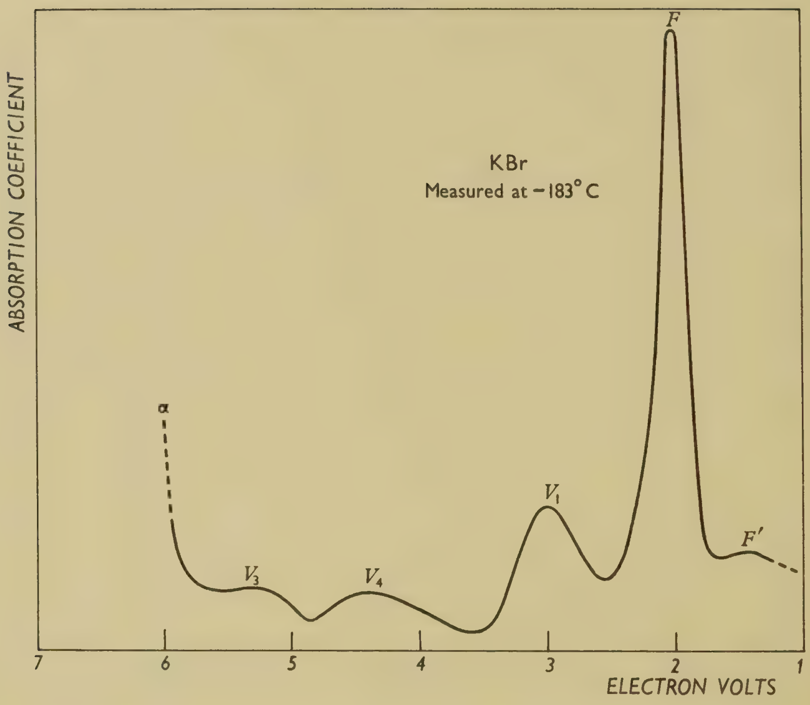


Fig. 6. ABSORPTION SPECTRUM OF POTASSIUM BROMIDE IRRADIATED WITH *X*-RAYS AT −183°C., SHOWING THE V_1, V_4 AND V_3 BANDS

clearly visible in published spectra. This has not been much studied, but in one detailed investigation was shown to maintain a constant ratio of intensity to the *F* band over a wide range of degrees of darkening.[74,233] It is therefore attributed to transitions from the ground state of the *F* centre to higher discrete excited states, occurring with relatively low probability[173,233] (see Fig. 8).

The small increment of energy required to raise an electron from the *2p* level into the conduction band is easily supplied thermally. Consequently a strongly temperature-dependent photoconductivity appears when *F* centres are illuminated with *F* light. At temperatures near that of liquid air, this photoconductivity practically disappears, but there is still a strong photoresponse in the *K* band, confirming the belief that the levels reached by absorption in this band lie very close to the conduction band or overlap it (see Fig. 8).

Several calculations of the energy levels of an *F* centre have been made.[133,240,259] The best of these give figures for the energy of the *1s–2p* optical transition within 0·1 e.V. of experimental values.[133]

The fact that the *F* band is a band, and not a sharp line, is a consequence of the broadening of the *2p* level by thermal lattice vibrations. The breadth of the band is given by the formula:-[173]

$$h\Delta\nu = \sqrt{h\nu_0 kT},$$

where $\Delta\nu$ = band width and ν_0 = a frequency of the same order as that of the band.

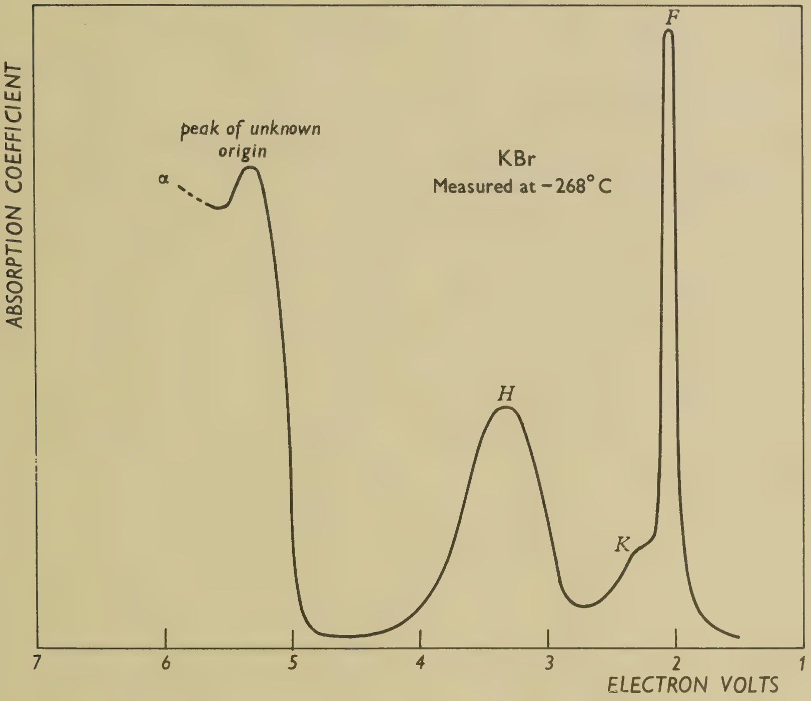


Fig. 7. ABSORPTION SPECTRUM OF POTASSIUM BROMIDE IRRADIATED AT −268°C., SHOWING THE *H* BAND

All the bands in the absorption spectrum of an irradiated alkali halide become broader with rising temperature. This hampers resolution of the bands to such a degree that in most recent investigations spectra have been measured at the temperature of liquid air or even at that of liquid hydrogen.

The concentration of *F* centres in a crystal can be determined from its optical absorption by a formula due to Smakula[242] (but see Seitz's comment[233]):-

$$N = \frac{18m}{\pi e^2 hf} \frac{n}{(n^2 + 2)^2} \alpha W$$

where N = number of F centres per c.c.; m = electron mass; e = electronic charge; h = Planck's constant; n = refractive index of crystal; W = width of the F band at half maximum, in electron volts; α = absorption coefficient of the crystal for light at the peak of the F band, in cm.$^{-1}$; f = oscillator strength of the F band. The value of f is approximately 1, since the band arises almost entirely from a single allowed transition. A more accurate value for potassium chloride, 0·81, has been obtained by directly measuring[123] the concentration of F centres in a crystal coloured by excess metal by dissolving it in water and estimating the OH^- formed in the reaction:-

$$e + H_2O \rightarrow OH^- + \tfrac{1}{2}H_2.$$

This concentration was used in conjunction with the measured optical absorption

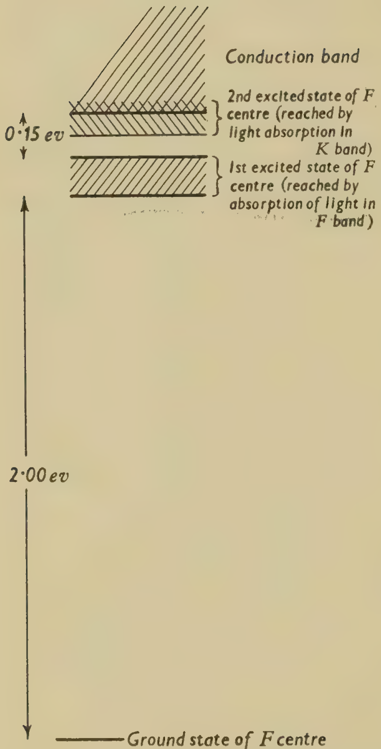

Conduction band
2nd excited state of F centre (reached by light absorption in K band)
0·15 ev
1st excited state of F centre (reached by absorption of light in F band)
2·00 ev
Ground state of F centre

Fig. 8. Energy Level Diagram of an *F* Centre in KBr

to determine *f* from Smakula's formula.

The bands other than the *F* band in an irradiated crystal have been divided (apart from the lattice bands; see page 2546) into trapped electron and trapped hole bands by the following argument. Since irradiation gives a hole for each electron excited and trapped, irradiated crystals show both electron and hole bands. In an unirradiated crystal containing excess metal, only electron bands can be present; in an unirradiated crystal coloured by excess halogen, only hole bands can be present. In this way the F', *R*, *M* and *N* bands have been identified as electron bands and the V_2 and V_3 bands as hole bands. The V_1, V_4 and *H* bands occur only in irradiated crystals, but are thought to be hole bands for less direct reasons (see page 2546).

The next electron band to be discussed is the F' band. It develops when the *F* band is irradiated with *F* light below a limiting temperature, which lies below room temperature for most of the alkali halides (see Table 1, page 2528). The interconversion of the *F* and F' bands is most easily studied in crystals containing excess metal, since in these it is not complicated by the partial bleaching of the bands owing to annihilation of electrons by holes (as happens in irradiated crystals). Fig. 2 (see page 2538) shows the *F* band in a potassium bromide crystal, coloured by excess metal, and the F' band formed when the *F* band is destroyed by prolonged illumination with *F* light at a suitable temperature. At temperatures where the quantum yields are a maximum, a quantum of *F* light destroys two *F* centres and produces one F' centre. The process is reversible: a quantum of F' light destroys one F' centre and produces two *F* centres. The only likely explanation of these yields is that the F' centre is an *F* centre which has captured an extra electron: the quantum of *F* light ionizes the electron off one *F* centre, and it is captured by another (forming an F' centre), so that two *F* centres are destroyed.

The R_1, R_2 and *M* centres are best considered together. The *M* band is often present in irradiated crystals and in those coloured by excess metal, without further treatment. It is enhanced by irradiation with *F* light at temperatures above the stability range of F' centres, and can be partly reconverted to the *F* band by irradiating it with *M* light. Whenever the *F* and *M* bands are interconverted in this fashion, they lose in intensity: at the same time the R_1 and R_2 bands appear between them and grow with each interconversion. Fig. 3 (see page 2539) shows this state of affairs. The *R* bands never appear in irradiated crystals until these have been treated with *F* or *M* light.

The constitution of the *R* and *M* centres has been elucidated by the following reasoning.[229] The *F* and *F'* centres exhaust the possibilities of trapping of electrons at a single vacancy. The *R* and *M* centres must therefore be built up on aggregates of vacancies. Now on thermodynamical grounds a large proportion of the vacancies in alkali halides are believed to be associated in pairs, a negative-ion vacancy with a positive-ion vacancy.[229] But there is probably no colour centre made up by trapping an electron at such a vacancy pair; for the energy changes involved are such that when the pair captures an electron it probably ejects a positive-ion vacancy, leaving an *F* centre.[229,233] The only remaining possibilities for two-vacancy electron centres are pairs of negative-ion vacancies which have captured respectively one and two electrons.[229] Those are identified with the R_1 and R_2 centres, for the following reason.[229] They resemble in electronic structure the H_2^+ and H_2 molecules; hence the arrangement of energy levels in the two centres can be predicted by analogy. This leads to the expectation that when either centre is raised to its first excited state by absorption of light, the vacancies would separate. With the increase of internuclear distance, the energy difference between ground and first excited states would become very small, and the system would make a spontaneous transition to the ground state. Consequently its lifetime in the excited state would be very short by comparison with, e.g., the life of an excited *F* centre, and it would be unlikely to receive the increment of thermal energy needed to take an electron into the conduction band. Therefore, these centres should exhibit no photoconductivity, and should not be bleached by light of the wave-lengths they absorb. This is, in fact, the reported behaviour of the *R* bands, though some doubts have recently arisen about their resistance to bleaching.

The two-vacancy centres just described have also been held responsible for some bands in the ultra-violet, so far described by only two groups of investigators, and unfortunately called the '*K* bands', though not, apparently, connected with the *K* band described earlier in this Section.[93,261,266]

The structure given for the *M* centre in Table 1 (see page 2528) is the simplest structure not already postulated for *F*, *F'*, R_1 or R_2 centres. It explains the properties of the *M* band very satisfactorily. The energy levels of a centre having the postulated structure have been calculated for LiCl and NaCl; in the former case, the calculated energy of the *M* band peak differs by 0·2 e.V. from the experimental value, and in the latter case the difference is much smaller.[111] The calculations predict a second excited state of the centre with a corresponding optical absorption band in the near ultra-violet; this has not yet been thoroughly searched for.[233] The fact that the *M* centre has less than cubic symmetry has been elegantly demonstrated in bleaching experiments with polarized light, which confirm the correctness of the model shown in Table 1.[267] The crystal was irradiated with *M* light polarized in one of its principal planes. The drop in the strength of the *M* band was greatest when the measurement was made with light polarized in the same direction as the bleaching light, showing that *M* centres with a particular orientation had been selectively bleached. A further strong argument for this *M* centre model is the fact that a simple and plausible mechanism involving the migration of vacancies will explain how *M* centres are formed as one of the first products of the photoionization of *F* centres.

The *N* band lies in the near infra-red. It is formed, like the *M* band, both by direct *X*-irradiation of the crystal, and also by the bleaching of *F* centres in crystals containing excess metal, but it is weaker than the *M* band. There is at present no reliable basis for choosing between several alternative structures.[233]

The 'colloid' band is a broad band in the visible caused by particles of metal of colloidal dimensions scattered through the crystal. These can be seen with the ultramicroscope. The condition arises most easily in crystals containing excess metal, and is developed by heating such crystals between about 250°C. and 500°C. for some time, and then quenching. There is an equilibrium between F centres and colloid particles of various sizes. At temperatures of the order of 600°C., essentially only F centres are present; the metal is completely 'dissolved'. With falling temperature the colloid band becomes stronger and the F band weaker, though the latter never disappears. Below about 250°C. equilibrium can no longer be reached in a measurable time. This makes it possible to 'freeze in' the equilibrium states corresponding to higher temperatures by sudden quenching to room temperature. It is seldom possible to generate the colloid band in irradiated crystals, for when these are heated to the temperature required for coagulation of the F centres (250–300°C.) they usually bleach completely, because the electrons released thermally from their traps are annihilated by positive holes. However, the colloid band is occasionally observed in crystals irradiated in atomic reactors.

The interconversion of colloids and F centres presumably proceeds by way of aggregates of intermediate size. The M centres are probably among these, since they are often observed in crystals quenched from high temperatures; but the R and N bands do not form in crystals heated above 300°C.[233]

The absorption spectrum of the colloids can be satisfactorily accounted for on the classical Mie theory of the scattering of light by small particles.[73,163,214,233]

The Lattice Bands.

The α and β bands (also called 'Greek' bands) will here be termed 'lattice bands' because they are caused by light absorption, not in the colour centres themselves, but in ordinary lattice anions whose environment is disturbed by vacancies or F centres generated by irradiation. The excited state reached when light is absorbed in either lattice band is the same as that attained by absorption in the first fundamental band of the crystal, but is perturbed by the adjacent vacancy or F centre. Consequently the α and β bands lie right on the edge of the first fundamental band (see Table V, page 2537), either close to or beyond the short wave limit of ordinary spectrophotometers.

The β band is present in crystals coloured by excess metal, and cannot therefore be a hole band. It is comparable in size with the F band (see Fig. 4, page 2540), and increases and diminishes in strict proportion to the F band when this is generated or bleached.[43,44] For this reason it is attributed to the absorption of light by a halogen ion immediately adjacent to an F centre.[233]

When F centres are converted to F' centres by irradiation with F light, the α band develops in proportion to the F' band. The spectrum shown in Fig. 4 is such as would be observed when the F band was partly converted to the F' band in this way. The α band disappears along with the F' band when the latter is destroyed by heating. It could, therefore, be connected either with the F' centres themselves, or with the halogen ion vacancies simultaneously formed when F centres are converted to F' centres. The latter explanation must be correct, for the α band is observed in circumstances in which the F' band is very weak or absent.[233] For example, it develops in crystals irradiated with X-rays at very low temperatures, which have practically no F' absorption. It has also been detected in the spectrum of a highly 'disordered' potassium iodide film made by condensing the vapour on a surface at -190°C.[47]

The Hole Bands (see Tables III and VI).

Apart from a few experiments some twenty years ago, the hole bands were not seriously studied until recently. Consequently the models for the hole centres shown in Table III are more controversial than those already discussed for the electron centres. One of the chief obstacles to the investigation of the hole centres is that the simplest, the antimorph of the *F* centre, (at present identified by Seitz with the V_1 centre) appears not to be stable much above liquid air temperature.

The V_2 and V_3 bands are probably the only bands stable at room temperature. They form under irradiation at room temperature, and can also be developed by absorption of halogen into the crystals at high temperatures. For reasons unknown, the latter method works only with bromides and iodides, and not with chlorides, though the bands can be developed in chlorides by irradiation. In the electrolysis of crystals at high temperatures, V_2 and V_3 centres form at the anode and migrate towards the cathode. These facts leave no doubt that the V_2 and V_3 bands are due to trapped holes. The centres responsible for these bands are believed (Seitz) to be built on *pairs* of positive ion vacancies, since the concentration of halogen (as V_2 and V_3 centres) in a crystal is found to be proportional to the first power of the pressure of the diatomic halogen gas around it.[169,170,233] In other words, they are probably antimorphs of the *R* centres. That having two trapped holes would be neutral, and should therefore easily be bleached by any free electrons in its vicinity. The other, however, with one trapped hole, would have a net negative charge, and should repel electrons and resist bleaching by them. Evidence that hole centres with these properties exist in *X*-irradiated crystals at room temperature is provided by the bleaching behaviour of *F* centres in such crystals. These *F* centres consist of a 'soft' component which bleaches easily under *F* light, and a 'hard' component which bleaches much more slowly.[233] It is not likely that there are really two different kinds of *F* centres; more probably, the rapid bleaching occurs while there are neutral hole centres available to accept the photoelectrons from the *F* centres, and the slow bleaching when only negative hole centres are left. Accepting the view that the V_2 and V_3 centres are antimorphs of the *R* centres, the next problem is to determine which of them has one trapped hole and which two. Unfortunately there have been no detailed studies to find which *V* band bleaches first when the *F* band is illuminated, but in work on thermal bleaching of irradiated potassium chloride, the V_2 band has been found to bleach faster than the V_3 band. Consequently the V_2 centre is provisionally assigned two holes and the V_3 centre one hole.[233]

Neither the V_1 nor the V_4 band (see Fig. 6) has been found with certainty in crystals coloured by excess halogen: they appear in crystals irradiated with *X*-rays at about liquid air temperature. The V_1 band is shaped like the *F* band; and V_1 centres, on irradiation with V_1 light at low temperatures, give only a small yield of free holes, which may be compared with the low photoconductive yield from *F* centres at these temperatures. Consequently the V_1 band is ascribed by Seitz to the antimorph of the *F* centre, *i.e.* a hole trapped at a positive ion vacancy.[233] The structure given for the V_4 centre in Table III is largely speculative at present.[233] Both V_1 and V_4 bands disappear on warming to room temperature.

It is not yet certain that the centres numbered V_1, V_2, V_3 and V_4 in potassium bromide have the same structures as those correspondingly numbered in potassium chloride.[233]

The *H* band (see Fig. 7) is a prominent band which appears instead of the V_1 band, and at nearly the same wave-length, when potassium chloride and bromide are *X*-rayed at the temperature of liquid hydrogen or liquid helium. It is not formed at liquid air temperature, and bleaches rapidly on warming to this temperature. Seitz has shown that his model for this centre (a hole trapped at a pair of vacancies of opposite sign) satisfactorily accounts for its instability.[233]

Impurities and the Formation of Colour Centres in the Alkali Halides.

Until recently, the potential importance of impurities in the formation of colour centres was insufficiently appreciated.[220] In typical investigations of colour centres, the concentrations of centres are of the order of 10^{16} to 10^{17} per c.c., similar to that for impurity atoms in the crystals, as shown by spectroscopic analysis and by ionic conductivity.[58,220]

Some investigators believe that an absolutely pure crystal would not darken at all when exposed to *X*-rays.[220] Even on a more conservative view, there remains the possibility that impurities may play an important part in the generation of colour centres. Unfortunately, the preparation of single crystals purer than the best used hitherto is a major experimental problem.[58] As an alternative approach, impurities have been deliberately added and their effects studied. These investigations have given two principal results. Firstly, impurities increase the rate of darkening of crystals under irradiation.[64,110,220,241] Both anionic impurities ($O^{=}$, $S^{=}$) and cationic impurities (Ca^{++}, Sr^{++}, Ba^{++}, Cd^{++}) have this effect.[220] In the presence of divalent anionic impurities, there must be extra anion vacancies equal in number to the impurity atoms in order to preserve electrical neutrality. This higher concentration of electron traps may account for the increased rate of formation of *F* centres. Similarly, a positive ion vacancy must be present for each divalent cation: these vacancies presumably trap holes formed by irradiation, so that the rate of recombination of holes and electrons is reduced, and *F* centres are formed more quickly. Secondly, the absorption spectra of crystals containing impurities show new absorption bands not found in the pure alkali halides. Some of these bands appear when the impurity is added, and others develop upon subsequent *X*-irradiation. A great deal of work has been carried out on the absorption spectra of phosphors made by adding traces of heavy metals to the alkali halides. This work is concerned only to a limited extent with the effects of ionizing radiation, so it will not be described here, but a full and up-to-date bibliography is available.[247] Here only the effects of adding hydride or alkaline earth ions will be discussed.

Alkali halides containing a few parts per million of hydride, and not further treated, show a strong ultra-violet absorption band, the *U* band.[2,104,105,107,124,155,156,158,165,196,257] This can also be seen in some published spectra of crystals coloured by excess metal, in which it arises from hydrogen impurity. Since the lattice constant of potassium bromide decreases linearly with the amount of hydride added, the hydride is believed to go into solid solution, H^- ions replacing Br^- ions in the lattice.[108,173] When the *U* band is illuminated with *U* light at room temperature it bleaches and the *F* band develops instead.[104,105,108,124,155,173,257] The quantum efficiency of this conversion at a given temperature is not the same for crystals containing deuteride as for those containing hydride; consequently the movement of atoms is thought to be involved in the process.[108,124,173] Light is probably absorbed in a hydride ion, exciting one of its electrons on to the neighbouring metal atoms.[173,233] The hydrogen atom remaining then diffuses out of its site, leaving a negative ion vacancy, which then recaptures the electron originally excited away to form an *F* centre. The same transformation can be brought about by *X*-rays at room temperature.[158,159] Below -100° C., irradiation with *X*-rays gives α-centres instead of *F* centres.[156] This can be explained only on the rather unsatisfactory hypothesis that the whole H^- ion leaves its site at low temperatures.[233]

Turning to the extra absorption bands observed in alkali halides containing calcium, strontium or barium ions, the wave-lengths of the band peaks are given in Table VII. Sodium chloride, with calcium or strontium added, coloured by excess metal and quenched, shows in addition to the usual *F* band a new band, Z_2, lying close to the *F* band.[190,231,286] Potassium chloride with the same impurities, but cooled slowly after colouring with excess metal, shows a similar band.[30,189,286]

Under F or Z_2 light these bands fade, and are replaced by the Z_1 band in the same spectral region.[26,27] Z_1 is not bleached by Z_1 light at room temperature.[26]

If sodium or potassium chloride containing the divalent impurities is irradiated with X-rays, only the F band develops, but this is converted to the Z_1 band, as in crystals coloured by excess metal, when it is irradiated with F light.[26,189,190] The formation and properties of the Z_1 band recall those of the R bands in 'pure' alkali halides. Seitz has proposed models for the Z centres.[231]

The Mechanism of Formation of Colour Centres.

To determine how colour centres are formed, it is necessary to know firstly, the source of the electrons and holes, and secondly, how the vacancies originate.

It is clear how electrons in the conduction band and holes can be trapped by vacancies. It is more surprising that F centres are formed, with a quantum yield at first approaching unity, by absorption of light in the first fundamental absorption bands of the alkali halides (see Table 1). Since this light does not cause photoconductivity, it must be assumed that excitons can also form F centres.[233] Presumably, when an exciton is captured at a halogen ion vacancy, the electron remains as an F centre and the hole moves away.[233] The high quantum efficiency of this process proves that excitons must migrate easily.[233]

The origin of the lattice vacancies required for colour centre formation has been much discussed. It now seems clear that they are in part present in the crystal before irradiation, but that many, often nearly all, of the colour centres develop in vacancies that are actually generated during irradiation. The vacancies present before irradiation arise from two causes: some are there to preserve electrical neutrality in the presence of divalent impurities: others may be there (if the crystal was grown from the melt) because alkali halides at their melting point contain about 10^{-4} mole fraction of vacant lattice sites in thermal equilibrium, and many of these become 'frozen in' as aggregates on cooling.[233,248] Seitz has outlined a sequence of events by which F, M and R centres could be generated following the trapping of electrons and holes at aggregates of vacancies.[229] This mechanism involves the migration of vacancies and vacancy pairs for short distances at room temperature, and is consistent with the activation energies for vacancy migration deduced from measurements of ionic conductivity and from theory.[229] It is certainly not possible, however, to account for all the phenomena of colour centre formation solely by means of vacancies already present in the unirradiated crystal. Table VIII gives colour centre concentrations up to 5×10^{19} per c.c. as obtainable by electron bombardment in single crystals of sodium and potassium chlorides; this is higher than any likely concentration of vacancies (the vacancy concentration in well-annealed sodium chloride has been estimated by comparing the actual density with the theoretical density computed from the X-ray lattice parameter and molecular weight: it is about 8×10^{18} vacancy pairs per c.c.).[233,248] This result suggests that many vacancies are produced during irradiation. This is convincingly proved by the recent discovery that alkali halides expand during irradiation. There is a decrease in density, and also an increase in linear dimensions. The data relating to volume changes are collected in Table VIII together with information on colour centre concentrations, where available. In the four investigations in which both colour centre concentration and expansion have been measured, the number of F centres per c.c., measured optically, agrees quite well with the number of extra vacancy pairs per c.c. generated during irradiation, as calculated from the volume change. The results of Sakaguchi and Suita show that the

TABLE VIII. - ENERGY CONSUMPTION AND MAXIMUM ATTAINABLE CONCENTRATIONS IN THE GENERATION OF *F* CENTRES

Reference and Date	Salt	Radiation	Whether irradiated to 'saturation'	Energy consumed per *F* centre formed (e.V.)	Limiting number of *F* centres per c.c.	Limiting number of vacancy pairs per c.c. and method of measurement
Pater (1951) *185*	KCl NaCl	electrons 5–15 kV.	Yes	–	$2{\cdot}85 \times 10^{19}$ $4{\cdot}58 \times 10^{19}$	–
Treitl (1953) *260*	KCl rock salt	electrons 10 kV.	Yes	–	$2{\cdot}9 \times 10^{19}$ 5×10^{19}	–
Estermann, Leivo and Stern (1949) *63*	KCl	soft *X*-rays	Yes	–	$6{\cdot}2 \times 10^{17}$ (average)	$11{\cdot}0 \times 10^{17}$ (average) (density)
Hacskaylo and Groetzinger (1952) *90*	NaCl	soft *X*-rays	Probably	–	–	$1{\cdot}8 \times 10^{18}$ in normal state $12{\cdot}8 \times 10^{18}$ in metastable state induced by electrolysis (density)
Hacskaylo and Otterson (1953) *91*	NaCl	soft *X*-rays	Probably	–	–	$2{\cdot}7 \times 10^{18}$ (density)
Hacskaylo, Otterson and Schwed (1953) *92*	NaCl	soft *X*-rays	Probably	–	–	$2{\cdot}5 \times 10^{18}$ (density)
Sakaguchi and Suita (1952) *212*	NaCl KCl KBr	soft *X*-rays	Yes	–	Within 30% of the number of vacancy pairs (estimate, Ref. *233*)	$\sim 1{\cdot}2 \times 10^{18}$ (Estimate quoted from Ref. *233*) (change of length)
Platt and Markham (1953) *194*	NaCl	soft *X*-rays	Yes	–	$\sim 2 \times 10^{18}$ (estimated very roughly from data given in this ref.)	–
Lin and Russell (1955) *142*	NaCl	soft *X*-rays	Probably not	–	$3{\cdot}9 \times 10^{16}$	$4{\cdot}1 \times 10^{16}$ (change of length)
Lin and Russell (1955) *142*	KCl	–	–	–	$2{\cdot}0 \times 10^{16}$ $6{\cdot}7 \times 10^{16}$	$\left.\begin{matrix} 2{\cdot}1 \times 10^{16} \\ 6{\cdot}6 \times 10^{16} \end{matrix}\right\}$ 2 crystals (change of length)

TABLE VIII (continued)

Reference and Date	Salt	Radiation	Whether irradiated to 'saturation'	Energy consumed per *F* centre formed (e.V.)	Limiting number of *F* centres per c.c.	Limiting number of vacancy pairs per c.c. and method of measurement
Harten (1949) *96*	KCl	hard *X*-rays	Yes	from 120 e.V. at room temperature to ~2000 e.V. at −183°C.	6×10^{16} at 20°C. 4×10^{16} at 60°C.	–
Schneider (1951) *218*	KCl	hard *X*-rays	No	initially 18 e.V., rising to about 53 e.V.	–	–
Mador, Wallis, Williams and Herman (1954) *149*	NaCl	hard *X*-rays	Yes	~100 e.V. early in the irradiation	7×10^{16} to 2×10^{17}, varying with sample	–
Alger and Jordan (1955) *2*	KBr	Co^{60} γ rays, *X*-rays	Yes	92-154 e.V., decreasing with temperature down to −193°C.	No figures given, but saturation *F* centre concentration increases with radiation intensity	–
Drexler *56*	rock salt	β-rays 130-450 kV.	–	6400 e.V.	–	–
Belar (1923-6) *14, 15*	rock salt	radium $\beta + \gamma$	Yes	–	up to about 10^{17}, increasing with intensity	–
Urbach (1926) *270*	natural KCl	radium $\beta + \gamma$	Yes	–	$\sim 0{\cdot}2 \times 10^{17}$	–
Leitner (1936) *136*	rock salt	hard *X*-rays Ra β-rays Ra γ-rays	No	~200 e.V. ~80 e.V. ~2000 e.V.	–	–
Primak, Delbecq and Yuster (1955) *199*	LiF	high energy deuterons	Not stated	–	2×10^{19}	$\sim 1{\cdot}2 \times 10^{19}$ (birefringence of non-uniformly irradiated LiF)
Leivo (1953) *137*	KCl	360 MeV. protons	Not stated	–	–	$\sim 4 \times 10^{17}$ (density)

TABLE VIII (continued)

Reference and Date	Salt	Radiation	Whether irradiated to 'saturation'	Energy consumed per *F* centre formed (e.V.)	Limiting number of *F* centres per c.c.	Limiting number of vacancy pairs per c.c. and method of measurement
Smoluchowski (1954) *109*	KCl	400 MeV. protons	Not stated	–	*F* centre concentration $\ll$ vacancy concentration after proton irradiation, but subsequent *X*-irradiation gives high density of *F* centres	$\sim 4 \times 10^{18}$ at 50°C. (density)
Wieninger and Adler (1950) *280, 281*	rock salt	α rays	Yes	About 4600 e.V. in early stages	$\sim 2 \times 10^{19}$	–

Note: All figures are for temperatures near room temperature unless otherwise stated.

expansion starts at the beginning of the irradiation, so that the generation of vacancies under irradiation probably occurs irrespective of the initial presence of vacancies in the crystal.[212,233] It should be noted that the expansion takes place under irradiation with soft *X*-rays, which cannot cause atomic displacements by elastic collision in appreciable numbers.[230] The generation of vacancies must therefore be a consequence of ionization or excitation or both. The most likely source of the vacancies is the edges of incomplete lattice planes (dislocations).[233] These planes can extend themselves by adding on at their edges ions derived from the neighbouring perfect crystal planes. The removal of ions from these perfect planes leaves vacancies, which at ordinary temperatures can diffuse away from the dislocation.[233] Seitz has suggested that the capture and annihilation of excitons at the dislocations would create 'thermal spikes' (*i.e.* localized regions of high temperature) which could cause vacancies to 'evaporate' from the region of the dislocation.[232,233] At liquid helium temperatures there is effectively no thermal diffusion, and the colour centres, if formed in this fashion, would be thickly clustered about the dislocation planes. Such clusters might be seen with the microscope, but no such searches have been reported.[233] The bleaching of colour centres formed at liquid helium temperature supports the belief that they are clustered.[152,232,233]

The mechanical properties of crystals are very sensitive to changes in their vacancy and dislocation pattern, and might be expected to change in consequence of irradiation if the ideas just described are well founded. Such changes do occur. The hardness of sodium chloride increases by a factor of two under bombardment by protons, electrons or *X*-rays.[79,273,277,278] Its yield stress and Young's modulus increase, and its internal friction diminishes.[71,79,81,195,197,273] These effects are attributed to the 'pinning' of dislocations by clusters of vacancies generated during irradiation. (See also refs. 150 and 186 for effects of irradiation on self-diffusion and ionic conductance).

Plastic flow increases the concentration of vacancies in alkali halides, as shown by an increase in the ionic conductivity. It also increases the rate of darkening by *X*-rays.[233,268]

Varley has described an alternative mechanism by which vacancies might be formed under irradiation; the consequences of this have not yet been fully examined.[271,272] Halogen ions might lose several electrons, so acquiring a positive charge, become unstable in their normal lattice positions for electrostatic reasons, and so be expelled into interstitial positions, leaving vacancies. The defects formed in this way are Frenkel defects, in contrast to the Schottky defects formed by the dislocation mechanism. It is possible to distinguish experimentally between these two types of defect by the kind of lattice expansion they cause.[17] If the defects are of Frenkel type, the proportionate change in X-ray lattice parameter should equal the proportionate change in linear dimensions of the crystal; if they are of Schottky type, the change in lattice parameter should be much smaller than the change in linear dimensions. Unfortunately, no comparison has yet been made of changes in density and X-ray lattice parameter on the same crystal, except for lithium fluoride (see page 2560) where the defects are probably the result of elastic collisions. But in the one study so far made of the change in lattice parameter in potassium chloride, this was found to be very much smaller than the change in linear dimensions observed by other workers under similar conditions, suggesting that Frenkel defects are few compared with Schottky defects.[16]

The studies so far published on the energy consumption in formation of F centres have not revealed any clear and consistent picture. Since the ionization threshold in the alkali halides is about 10 e.V., and the energy of an exciton is rather less than this, one would expect a yield of the order of one F centre per 10 e.V. if the energy expended in the crystal were fully utilized. Some actual results on 'pure' alkali halides are given in Table VIII. These show that the hypothetical maximum efficiency is never achieved, but the variations in actual energy consumption per F centre are enormous. This is not surprising when it is remembered that relatively slow thermal processes (the diffusion of vacancies) are involved in the formation of colour centres, and that spontaneous thermal bleaching, and bleaching by the radiation itself, take place while the centres are being formed.

With regard to the kinetics of F centre formation, there is general agreement about the following facts. The rate of formation of centres drops as irradiation continues, a 'saturation' or 'limiting' concentration eventually being attained. This limiting concentration increases with the intensity of the radiation: the increase has been directly demonstrated in the experiments of Belar and of Alger and Jordan (see Table VIII), and is also evident in the fact that the highest concentrations of F centres recorded have been achieved with the least penetrating radiations (cathode rays, soft X-rays and deuterons – see Table VIII), which give the highest local rates of energy absorption. The rate of formation of F centres drops with temperature between +60°C. and −253°C.[96] The drop is at least partly due to the fact that, at temperatures well below room temperature, α centres form, instead of F centres, in such numbers that the total production of centres of both types varies little with temperature.[157] This is an interesting demonstration that the formation of negative ion vacancies by irradiation, and their filling with electrons, are essentially independent processes.

An upper limit is set to the concentration of colour centres obtainable under irradiation by the fact that the trapped electrons can 'tunnel' through to the trapped holes, and annihilate them, when the two types of centre are close enough together.[229,233] Calculation shows that 'tunnelling' should become important in the concentration range 10^{19} to 10^{20} centres per c.c.[154,233] The highest concentrations of F centres experimentally attained (by cathode ray bombardment of potassium chloride – Table VIII) are about 5×10^{19} per c.c., corresponding to a degree of 'decomposition' of about 0·3%. Halogen could escape only from the surface layers of an irradiated crystal, so that there is usually no appreciable change in the bulk composition of a crystal during irradiation, and the crystal returns to its original chemical state when bleached by heating. However, intense surface irradiation of lithium, sodium and potassium chlorides with protons does leave a film of metal, presumably owing to loss of halogen.[33,128]

Band Wave-lengths and Lattice Constant.

Several empirical relationships between the lattice constants of the alkali halides and the wave-lengths or frequencies of the various colour centre peaks have been suggested.[113,114,168,213] The most recent work is by Sauvenier, who[213] has critically examined earlier proposals. He states that the equation $Ed^n = C$, where E is the energy of band peak in electron volts, d the lattice parameter in A., and C and n are constants, fits well the experimental data on F, M, α, U and R_2 bands. Values of n in the neighbourhood of 2·1, and of C near 21, fit the F bands and R_2 bands in all the halides. For the M and U bands, n is about 1, and for the α bands about 0·2. Sauvenier's paper includes a table of the best values of n and C for the bands mentioned, in various groups of alkali halides.

Chemical Behaviour of Irradiated Alkali Halides.

In one series of investigations, solutions of irradiated sodium chloride in water have been shown to be slightly alkaline and to have oxidizing power.[91,92] This behaviour may evidently be described in terms of the presence of 'free sodium' and 'free chlorine' in the crystals, but these terms are hardly legitimate, since the colour centres are not identical with sodium atoms and chlorine molecules. The reactions taking place upon dissolution are probably:-

$$\left.\begin{array}{ll}(1) & e + H_2O \rightarrow OH^- + H \\ (2) & h + Cl^- \rightarrow Cl\end{array}\right\} \times 4$$

(where h represents a positive hole) giving equal numbers of hydrogen and chlorine atoms. (For discussion of the subsequent reactions, it is convenient to quadruple both these equations). A hydrogen atom stands equal chances of finding another hydrogen atom or a chlorine atom. The following equations therefore represent the formation of secondary products in the correct proportions:-

$$\begin{array}{ll}(3) & H + H \rightarrow H_2 \\ (4) & 2H + 2Cl \rightarrow 2H^+ + 2Cl^- \\ (5) & 2Cl + H_2O \rightarrow H^+ + Cl^- + HOCl.\end{array}$$

The four OH^- ions from (1) are then neutralized, three of them by H^+ ions from (4) and (5) and the other by the HOCl from (5). The end products are therefore $H_2 + 3Cl^- + ClO^-$. The ClO^- is responsible both for the oxidizing power and for the alkalinity of the solution (the latter because hypochlorous acid is very weak and the reaction $ClO^- + H_2O \rightarrow HOCl + OH^-$ is appreciable). If this scheme is correct, there should be two equivalents of oxidizing power for every four trapped electrons, and a comparatively small amount of alkalinity determined by the dissociation constant of hypochlorous acid. The actual numbers of colour centres were not determined in this work, but the numbers of vacancy pairs generated during irradiation were estimated from the change of crystal density. The results for strongly X-irradiated sodium chloride were:-

$25 \pm 6 \times 10^{17}$ vacancy pairs per c.c.
$15 \pm 4 \times 10^{17}$ 'free chlorine atoms' per c.c.
3×10^{17} 'free sodium atoms' per c.c.

If we make the plausible assumption (to some extent supported by data in Table VIII) that the number of trapped electrons equals the number of vacancy pairs, the trapped electrons stand in about the expected ratio to the oxidizing power. The alkalinity ('free sodium atoms') is also present in about the expected amount.

There are no other detailed reports on the chemical behaviour of irradiated alkali halides. In general one would expect the trapped electrons to reduce any reducible substances present during dissolution, and the holes to oxidize any oxidizable substances present. The electrons and holes might also initiate polymerization in solutions of monomers.

EFFECTS OF ELECTRONIC EXCITATION AND IONIZATION IN SALTS CONTAINING COMPLEX ANIONS

Colour Centres.

Centres analogous in structure to those described for the alkali halides would be expected to form, during irradiation of salts containing complex anions, by the trapping of electrons and holes at lattice vacancies. The wave-length of the *F* band in the alkali halides depends mainly on the lattice constant; consequently the *F* band in salts of the formula MX (M = an alkali metal, X = a univalent anion other than halide ion) should fall somewhere near the *F* bands in alkali halides with similar lattice constants.[99,112,115a,240] *X*-Irradiated sodium cyanide shows a band at 5100 A. which is in the correct position for an *F* band, and another at 3600 A. which may well be a *V* band.[112] Potassium azide irradiated with ultra-violet light is blue, and this is consistent with the presence of *F* centres.[115a] Potassium borohydride quickly becomes bright blue when irradiated with *X*-rays, probably because of *F* centres.[100] Sodium azide and sodium nitrate, after irradiation with *X*-rays, exhibit a number of absorption bands, the causes of which have not been determined.[99,140,202]

Decomposition of the Anion: General.

This type of decomposition, which is quite common, involves the breaking of covalent bonds. It differs from the formation of colour centres in not being reversible by heating or tunnelling of electrons as a rule, so that the salt may decompose completely if irradiated long enough.

Nothing is known of the actual mechanism of any decomposition of this kind, but the following important possibilities may be mentioned:-

(1) Dissociation of electronically excited anions. This would probably take place chiefly at lattice defects, for the following reason. Excitons in the salts under discussion, as in the alkali halides, would probably be mobile and might be expected (see page 2523) to spend about 10^{-15} second on each anion before passing on to the next. This interval is too short to allow the excited anion to dissociate, since bond oscillations have periods of the order of 10^{-13} second. Consequently no dissociation would be expected until the exciton is brought to rest, *i.e.* trapped at a lattice defect. Although there is no information on this process in crystals subjected to ionizing radiation, it is worth mentioning here that the decomposition of azides by ultra-violet light involves the reaction of pairs of excitons trapped (probably) at vacant cation sites.[115,258]

(2) Dissociation of the anion radicles (e.g. NO_3 in a nitrate) generated by the removal of electrons from anions. Such a radicle can be regarded as an anion plus a positive hole. These dissociations might also take place at lattice defects to which the holes have migrated.

If the fragments of a dissociating anion or anion radicle are not to recombine, it would be necessary in many cases for one of the fragments to move away from the site of dissociation. In a region of perfect lattice, this could be done only by forcing one of the fragments into an interstitial position. This might well require more energy than is available from the electronic excitation. At a lattice vacancy, however, the fragment could move into an empty space, and the dissociation would require less energy. This factor alone may restrict some decompositions to the neighbourhood of lattice defects.

Experimental Data on the Decomposition of Anions.

The quantitative information on this subject is given in Table IX. There and in this Section is given the little available information on radiation decomposition of anions of salts other than those of the alkali metals.

TABLE IX. - QUANTITATIVE INFORMATION ON THE RADIATION DECOMPOSITION OF SALTS WITH POLYATOMIC ANIONS

Author and Date	Ref.	Salt	Radiation	Decomposition Products	*G* value (mols. product/ 100 e.V.)	Influence of temperature
Hennig, Lees and Mathieson (1953)	*102*	$NaNO_3$	Pile, slightly above room temperature	Principally nitrite and oxygen: a trace of nitrogen	$G(O_2)=0{\cdot}27$ (mean)	Not known
Hennig, Lees and Mathieson (1953)	*102*	$NaNO_3$	*X*-rays, *ca.* room temperature	Principally nitrite and oxygen: a trace of nitrogen	$G(O_2)=0{\cdot}32$ (mean)	Not known
Cunningham and Heal (1955)	*38*	$NaNO_3$	*X*-rays, 17°C.	Principally nitrite and oxygen: a trace of nitrogen	$G(NO_2^-) = 0{\cdot}43$	Not known
Hennig, Lees and Mathieson (1953)	*102*	KNO_3	Pile, slightly above room temperature	Principally nitrite and oxygen: a trace of nitrogen	$G(O_2)=0{\cdot}86$ (mean)	Not known
Cunningham and Heal (1955)	*38*	KNO_3	*X*-rays, 17°C.	Principally nitrite and oxygen: a trace of nitrogen	$G(NO_2^-) = 1{\cdot}75$	Rate of decomposition slightly greater at −75°C. and −180°C. than at 17°C.
Allen and Ghormley (1947)	*3*	$Ba(NO_3)_2$	Van de Graaff electrons	Principally nitrite and oxygen: a trace of nitrogen	$G(O_2)\cong 0{\cdot}1$ (figure given in ref. *102*)	Not known
Hennig, Lees and Mathieson (1953)	*102*	$KClO_3$	Pile, slightly above room temperature	Oxygen, (other products not identified)	$G(O_2)=2{\cdot}2$	Not known
Sharman and McCallum (1955)	*236*	$NaClO_3$	Pile, somewhat above room temperature	Mostly chloride, some perchlorate	-	Not known

TABLE IX (continued)

Author and Date	Ref.	Salt	Radiation	Decomposition Products	*G* value (mols. product/ 100 e.V.)	Influence of temperature
Heal (1953)	*98*	$KClO_4$	*X*-rays 25°C.	Mostly ClO_3^-, some Cl^-, small amounts of other Cl oxyanions	$G(ClO_3^-) \cong 4$ $G(Cl^-) \cong 1$	Not known
Boyd, Cobble and Wexler (1952)	*19, 32*	$KBrO_3$	Pile at 80°C.	Lower oxidation states of bromine (not further examined)	-	-
Boyd, Cobble and Wexler (1952)	*19, 32*	$KBrO_3$	γ-rays	Lower oxidation states of bromine (not further examined)	~1·5 bromate ions decomposed per 100 e.V.	Rate independent of temperature
Heal (1953)	*99, 100*	NaN_3	*X*-rays	Nitrogen. Aqueous solution also contains ammonia and hydroxyl ion	$G(N_2) = 6{\cdot}0$ (*100*)	Rate at 102°C. 1·3 times rate at 51°C. Rate at -180°C. 0·67 times rate at 17°C.

Note: '*G*' (coloumn 6) is the customary symbol used to denote the number of molecules of product formed per hundred electron volts absorbed by the compound.

Azides.

Sodium azide crystals turn brown when exposed to *X*-rays at temperatures from room temperature up to 102°C., and pale green if irradiated below room temperature[99,100] (see also the *X*-ray decomposition of barium azide[87]). The green crystals turn brown on standing for an hour or two at room temperature. When about 10% decomposed, the crystals are opaque even in thicknesses of about 0·1 mm.[100] The cause of the brown colour is an absorption band having a peak at 340–360 mμ and extending into the visible region.[99,140] To judge from its wave-length, this band cannot be due to *F* centres or to colloidal metal, and may be a hole band.

When irradiated sodium azide dissolves in water or in anhydrous ammonia, nitrogen is evolved.[99] The aqueous solution contains ammonia, hydroxyl ion, and a trace of hydrazine, as well as undecomposed azide.[99] The yields of nitrogen, hydroxyl ion and ammonia are in the ratio 4:3:1 moles.[99] There are several ways of accounting for this ratio: for example, decomposition to nitride and nitrogen:-

$$3N_3^- \rightarrow N^{3-} + 4N_2$$

followed by:-

$$N^{3-} + 3H_2O \rightarrow NH_3 + 3OH^-$$

or decomposition to sodium metal and nitrogen: $NaN_3 \rightarrow Na + \frac{3}{2}N_2$

followed by reduction of some of the undecomposed azide ion to ammonia by the sodium as the crystal dissolves.[99] There is some independent support for the latter explanation.[100] When the irradiated crystals dissolve in acidified 5% mercuric chloride solution, mercurous chloride is precipitated in about one third of the amount to be expected if all the sodium presumably formed in the decomposition were effective in reducing mercuric chloride. The remaining sodium must react with azide ion. The solution obtained from irradiated sodium azide and liquid ammonia at −78°C. has the characteristic blue colour of sodium-ammonia solutions. This colour disappears on warming to −33°C., presumably because the sodium then reacts with azide ion.

No nuclei of massive sodium metal can be seen in irradiated sodium azide under the microscope, and the absorption spectrum shows no evidence of colloidal metal or of *F* centres.[99] The only remaining possibility seems to be that the metal (or trapped electrons), which the chemical evidence shows to be present, exists in the form of small aggregates of electrons (perhaps like the *M* centres in alkali halides) which absorb in the infra-red.

The amount of sodium azide decomposed is proportional to the energy absorbed and independent of the dose rate.[99,100] The energy is very efficiently utilized (see Table IX). The temperature coefficient of the decomposition rate is small.[99,100] The decomposition of potassium and barium azides by **ultra-violet light**, which has been shown to proceed via the reaction of pairs of trapped excitons, has entirely different characteristics: the rate is proportional to the square of the light intensity, the quantum yield is low and the temperature coefficient high[115,258] (cf. decomposition by slow electrons[85]). Hence the *X*-ray decomposition must have a different mechanism, probably a simple dissociation of anion radicles.

Potassium bromate.

This salt is easily decomposed by pile or gamma radiation, giving lower oxidation states of bromine in amounts proportional to the dose and independent of temperature.[19,32] The decomposition products, probably hypobromite and bromide, were estimated together by reduction to bromide and titration with silver nitrate, so that the relative yields are not known (see Table IX).

Sodium and Potassium Chlorates (see Table IX).

Potassium chlorate decomposes when irradiated with cathode rays, in the pile, or with *X*-rays, with large yield.[102,246] Chloride and hypochlorite have been identified among the decomposition products.[246] The oxygen formed at the same time remains trapped in the crystals, setting up stresses so that crystals, 4% decomposed, decrepitate when disturbed.[102] Sodium chlorate decomposes in the pile much more slowly than the potassium salt (compare sodium and potassium nitrates).[236] The principal product is chloride, but there is also an appreciable amount of perchlorate formed.[236] Nothing is known of the kinetics or mechanism in either case.

Potassium Perchlorate.

The *X*-ray decomposition has been studied in some detail.[98] Chlorate and chloride are the principal products, but there are smaller amounts of other oxidizing substances, probably hypochlorite and chlorite. In the early stages the production of chlorate is about four times the production of chloride. When about 16% decomposed the crystals burst to a fine powder in consequence of the pressure of occluded oxygen; the rate of chloride production then doubles, while the rate of chlorate production remains unchanged. This is the only evidence so far obtained of a decomposition rate varying with the degree of crystalline perfection: in view of the probable importance of vacancies in decomposition, it is likely that other examples remain to be discovered. The chlorate formed in the decomposition itself decomposes to chloride in a secondary reaction (see Table IX).

Nitrates.

Under irradiation these decompose principally to nitrite and oxygen. The reaction was first observed in sodium nitrate bombarded with cathode rays.[246] It has since been shown to take place in barium nitrate irradiated with fast electrons,[3] in sodium nitrate irradiated in the pile or by *X*-rays,[102] and in potassium nitrate in the pile or under *X*-rays.[38,102] The oxygen formed is trapped in the crystals during the early stages of decomposition.[102] With potassium nitrate it begins to escape when the compound is between 20 and 30% decomposed, at room temperature.[38] Barium nitrate retains all its occluded oxygen up to at least 21% decomposition,[3] and sodium nitrate up to at least 1%.[102] The oxygen can be released by dissolving the crystals in water or by heating them. It comes off rapidly from potassium nitrate at the transition temperature (129°C.), but is released from sodium nitrate only at the melting point.[102]

The magnetic susceptibility of the trapped oxygen shows it to be present as ordinary O_2 molecules.[102] It is collected into small pockets in which the pressure may exceed 1000 atmospheres. The pockets are at first submicroscopic in size, and the crystals remain transparent. But samples which have been irradiated for a long time, or allowed to get warm, become opaque and milky in appearance because of the coalescence of the small gas pockets to larger ones visible in the microscope. When irradiated sodium nitrate is heated for some minutes between 255°C. and 302°C. the pockets coalesce further and the crystal expands considerably.[102]

The oxygen formed is approximately equivalent in quantity to the nitrite, but in published results never exactly so. The difference is undoubtedly due to side reactions. The oxygen evolved from the crystals contains a little nitrogen, and aqueous solutions of irradiated potassium nitrate are more alkaline than would be expected from hydrolysis of the nitrite.[288] The gas evolved when irradiated barium nitrate dissolves in water contains hydrogen, probably derived from the reaction of trapped electrons with water (cf. page 2554).[3]

The decomposition of potassium nitrate by *X*-rays seems to be a first order reaction, indicating no appreciable back-reaction between the nitrite and the occluded oxygen.[38] On the other hand, the dose-decomposition curve for barium nitrate gives grounds for thinking that the decomposition of this salt may not exceed about 40% even in very long irradiations.[3]

The absorption spectrum of irradiated sodium nitrate shows the expected absorption band at 345 mμ due to nitrite ions, and another at 335 mμ believed to be due to a colour centre.[202]

If the nitrates decompose thus:-

$$NO_3^- \rightarrow NO_2^- + O$$

it becomes a question how the oxygen atoms come together to form molecules. At least two alternative postulates are possible. The oxygen atoms may diffuse through a series of interstitial positions to the incipient gas pockets and there unite; or perhaps the actual dissociation takes place mainly at lattice defects (following migration of excitons or holes to these) and the gas pockets build up round the defects.

It is interesting that the quantum yields for decomposition by ultra-violet light of the three solid nitrates mentioned fall in the same order as the G values for decomposition by ionizing radiation (see Table IX).[51,132,177]

Other Salts.

The information on these is fragmentary. Potassium chromate is very resistant to decomposition by pile radiation,[147] as are potassium and lithium sulphates,[102] but sodium sulphate is reported to decompose under cathode ray bombardment.[246] Potassium ferrocyanide, irradiated in the pile, gives some ferric ion.[284] Ammonium hexafluoantimonate(V) decomposes to antimony(III) in the pile.[284] The phosphates of the alkali and alkaline earth metals decompose under β- and γ-irradiation to give phosphorus in lower oxidation states.[109] Silver acetylide, under electron bombardment, gives silver metal.[175]

NUCLEAR REACTIONS IN THE SALTS OF THE ALKALI METALS

Lithium Fluoride.

When bombarded with thermal neutrons, lithium undergoes the reaction:-

$$^{6}\mathrm{Li} + {}^{1}n \rightarrow {}^{4}\mathrm{He} + {}^{3}\mathrm{H} + 4{\cdot}8\ \mathrm{MeV.}$$

The large amount of energy produced is dissipated within the crystal in the form of excitation, ionization and elastic collisions caused by the helium and tritium nuclei, which leave the site of the reaction with kinetic energies of 2·06 MeV. and 2·74 MeV. respectively. This reaction makes it possible to obtain abnormally high rates of energy deposition per unit volume in lithium fluoride, as compared with halides of the other alkali metals: it is consequently worth while to look for the effects of elastic collisions, which are capable of displacing a substantial fraction of the atoms in the crystal in irradiations of a few hours' duration. The *X*-ray diffraction lines of lithium fluoride crystals broaden considerably in pile irradiations, suggesting extensive lattice damage.[120,275] It is not yet clear what form this damage takes. Binder and Sturm found that the density of lithium fluoride decreases, and that there is an equivalent increase in the average lattice spacing as determined by *X*-ray diffraction.[17] This result, if correct, indicates that the defects produced are Frenkel defects (*i.e.* interstitial atoms and vacancies) in the main. On the other hand, Keating has interpreted his results on the *X*-ray diffraction pattern to mean that there is no important concentration of interstitial atoms and vacancies, but that large regions of the irradiated crystal are in a state of uniform compression or expansion.[120] Until more experimental data have been collected, and their interpretation more fully considered, it will not be possible to state definitely how the structure of lithium fluoride changes on neutron irradiation, or what proportion of the damage is due to collision displacements.

The absorption spectrum of irradiated lithium fluoride shows an *F* band and a number of other bands which have been identified with the *F'*, *R* and *M* bands of the kinds observed with other alkali halides. There are, however, also a number of very sharp absorption lines superposed on the bands; the cause of these is not known, but the presence of rare earth impurities has been suspected.[201] (See also the references given in the second column of Table I, page 2528).

The Szilard-Chalmers Effect in Salts of the Alkali Metals with Polyatomic Anions.

The nuclear reactions of the alkali metals themselves are dealt with elsewhere in this volume, and it is here necessary to discuss only reactions in the *anions* of salts of the alkali metals. These reactions are conveniently divided into two categories: those giving a product isotopic with the target element (covered in this sub-section); and those giving a product not isotopic with the target element (see page 2565).

Szilard and Chalmers first noticed, in 1934, that the radioactive iodine obtained by neutron bombardment of ethyl iodide was mostly in a different chemical state (viz., elementary iodine) from the starting material.[251] It could therefore be separated chemically from the latter to give radioactive iodine of very high specific activity (*i.e.* diluted very little with inactive iodine). The chemical state of the iodine changes because the γ-quantum emitted in the activating (n,γ) reaction causes a recoil of the iodine atom vigorous enough to break its bond to the ethyl group. A great many other instances of this effect have since come to light. In many of these the activated atom is the central atom of a polyatomic anion (usually an oxyacid anion) in the salt of an alkali metal. These cases are listed in full in Table X, with references and an outline description of the effects observed. Since every example of the Szilard-Chalmers effect poses its own distinctive problems, usually extremely complex, reference should be made to the original papers for detailed information. A recent review can be recommended.[283] Here only a few generalizations, applicable to polyatomic anions, will be made.

TABLE X.- THE SZILARD-CHALMERS EFFECT IN SALTS OF THE ALKALI METALS

(γ,n) Reactions as well as (n,γ) reactions are included in this Table

Author and Date	Ref.	Compound	Reaction	Results*
Sharman and McCallum (1955)	*237*	Na_2CO_3(anhyd.)	$^{12}C(\gamma,n)^{11}C$	CO_2, CO, formic, oxalic, glyoxylic and glycollic acids
Rowland and Libby (1953)	*211*	Na_2CO_3(soln.)	$^{12}C(\gamma,n)^{11}C$	CO only formed – no CO_2
Rowland and Libby (1953)	–	$NaHCO_3$(solid)	$^{12}C(\gamma,n)^{11}C$	CO and CO_2 in about equal amounts
Rowland and Libby (1953)	–	$NaHCO_3$(soln.)	$^{12}C(\gamma,n)^{11}C$	CO only – no CO_2
Libby (1940)	*141*	$Na_2HPO_3, 5H_2O$	$^{31}P(n,\gamma)^{32}P$	Retention 92% (as phosphite)
Aten, van der Straaten and Riesebos (1952)	*11*	$Na_2HPO_3, 5H_2O$	$^{31}P(n,\gamma)^{32}P$	Retention 75%, remainder as ortho- and pyrophosphate
Libby (1940)	*141*	$Na_2HPO_4, 12H_2O$†	$^{31}P(n,\gamma)^{32}P$	Retention 52%
Aten, van der Straaten and Riesebos (1952)	*11*	$Na_2HPO_4, 2H_2O$	$^{31}P(n,\gamma)^{32}P$	Retention 22%, 59% phosphite and hypophosphite, remainder pyrophosphate
Aten, van der Straaten and Riesebos (1952)	*11*	Na_2HPO_4 (anhyd.)	$^{31}P(n,\gamma)^{32}P$	Retention 23%, 55% phosphite and hypophosphite, remainder pyrophosphate
Libby (1940)	*141*	$Na_3PO_4, 12H_2O$	$^{31}P(n,\gamma)^{32}P$	Retention 50%
Daudel (1942)	*41*	Na(?)arsenate	$^{75}As(n,\gamma)^{76}As$	Retention 50%, remainder as arsenite
Süe (1948)	*249*	Na_2HAsO_4	$^{75}As(n,\gamma)^{76}As$	Product arsenite, retention 40-50%
Süe (1948)	*249*	$NaAsO_2$	$^{75}As(n,\gamma)^{76}As$	90% Retention as arsenite, remainder to arsenate
Süe (1948)	*249*	$(CH_3)_2AsO_2Na$	$^{75}As(n,\gamma)^{76}As$	70-80% Recovery as arsenite and arsenate
Daudel (1942)	*41*	Na(?)antimonate	$^{123}Sb(n,\gamma)^{124}Sb$	No antimonite Retention complete
Daudel (1941)	*40*	Na_2SeO_3	$^{80}Se(n,\gamma)^{81}Se$	Complete recovery as elementary selenium

TABLE X (continued)

Author and Date	Ref.	Compound	Reaction	Results*
Daudel (1942)	*41*	$Na(?)_2SeO_4$	$^{80}Se(n,\gamma)^{81}Se$	Complete recovery as elementary selenium
Daudel (1942)	*41*	$Na(?)_2TeO_4$	$^{130}Te(n,\gamma)^{131}Te$	Complete recovery as elementary tellurium
D'Agostino (1935)	*39*	$NaClO_3$(solid)	$^{37}Cl(n,\gamma)^{38}Cl$	Product Cl^-
McCallum and Holmes (1951)	*143*	$NaClO_3$(solid)	$^{35}Cl(\gamma,n)^{34}Cl$	Product Cl^- Retention small
Sharman and McCallum (1955)	*236*	$NaClO_3$(solid)	$^{35}Cl(n,\gamma)^{36}Cl$	Product mainly Cl^-, some ClO_4^-. Retention 13%
D'Agostino (1935)	*39*	$NaClO_3$(soln.)	$^{37}Cl(n,\gamma)^{38}Cl$	Product Cl^-, effectively no retention
Libby (1940)	*141*	$NaClO_3$(soln.)	$^{37}Cl(n,\gamma)^{38}Cl$	Product Cl^-, effectively no retention
D'Agostino (1935)	*39*	$NaClO_4$(solid)	$^{37}Cl(n,\gamma)^{38}Cl$	Product Cl^-
Daudel (1942)	*41*	$Na(?)ClO_4$ (solid)	$^{37}Cl(n,\gamma)^{38}Cl$	Activity recoverable as Cl° or Cl^-
D'Agostino (1935)	*39*	$NaClO_4$(soln.)	$^{37}Cl(n,\gamma)^{38}Cl$	Product Cl^-
Libby (1940)	*141*	$NaClO_4$(soln.)	$^{37}Cl(n,\gamma)^{38}Cl$	Product Cl^-. Retention small
Libby (1940)	*141*	$NaBrO_3$(solid)	$^{79}Br(n,\gamma)^{80}Br$	Product Br^-. Retention small
Libby (1940)	*141*	$NaBrO_3$(soln.)	$^{79}Br(n,\gamma)^{80}Br$	Product Br^-. Retention small (except when solns. acidified)
Boyd, Cobble and Wexler (1952)	*19, 32*	$KBrO_3$(solid)	$^{81}Br(n,\gamma)^{82}Br$	Product Br_2. Retention from 9% upwards increased by heat or γ-radiation
Cleary, Hamill and Williams (1952)	*31*	$NaIO_3$(solid)	$^{127}I(n,\gamma)^{128}I$	Product I^-. Retention about 70%, increases on heating
Cleary, Hamill and Williams (1952)	*31*	$NaIO_3$(soln.)	$^{127}I(n,\gamma)^{128}I$	Product I^-. Retention about 20%
Cleary, Hamill and Williams (1952)	*31*	KIO_3(solid)	$^{127}I(n,\gamma)^{128}I$	Product I^-. Retention about 70%
Cleary, Hamill and Williams (1952)	*31*	$KH(IO_3)_2$(solid)	$^{127}I(n,\gamma)^{128}I$	Product I^-. Retention about 53%
Cleary, Hamill and Williams (1952)	*31*	NH_4IO_3(solid)	$^{127}I(n,\gamma)^{128}I$	Product I^-. Retention about 31%, increases on heating

TABLE X (continued)

Author and Date	Ref.	Compound	Reaction	Results*
Daudel (1942)	*41*	$NaIO_4$(solid)	$^{127}I(n,\gamma)^{128}I$	Product I^0 or I^-
Cleary, Hamill and Williams (1952)	*31*	$NaIO_4$(soln.)	$^{127}I(n,\gamma)^{128}I$	Product mostly IO_3^-; but if methanol present, chiefly I^-. Retention 6%
Muxart, Daudel, Daudel and Haissinsky (1947)	*176*	$K_2Cr_2O_7$(solid)	$^{50}Cr(n,\gamma)^{51}Cr$	No separation as Cr^{+++} (retention complete)
Green and Maddock (1949)	*83*	$K_2Cr_2O_7$(solid) K_2CrO_4(solid)	$^{50}Cr(n,\gamma)^{51}Cr$	Retention 88%, independent of pH of solvent soln. Retention a minimum, 55%, at pH 2. Increased by heating
Green, Harbottle and Maddock (1953)	*94*	K_2CrO_4(solid) K_2CrO_4 in solid soln. in K_2SO_4	$^{50}Cr(n,\gamma)^{51}Cr$	Retention constant at about 70% for solvent solns. of pH between 0 and 12. Increased by heating Retention nearly the same as in pure K_2CrO_4
Fishman and Harbottle (1953)	*68*	$\left.\begin{array}{l}Na_2CrO_4\\(NH_4)_2CrO_4\end{array}\right\}$ solutions	$^{50}Cr(n,\gamma)^{51}Cr$	Retention from 19 to 80%, a complicated function of pH
Kahn, Friedman and Bryant (1935)	*118*	$\left.\begin{array}{l}K_2Cr_2O_7\\\text{and } K_2CrO_4\end{array}\right\}$ solid	–	(Not stated)
Libby (1940)	*141*	$KMnO_4$(solid)	$^{55}Mn(n,\gamma)^{56}Mn$	Recovery as MnO_2 by adding Mn^{++} to soln. Retention ~30% at pH 1-10, rising at either extreme
Drehmann (1941)	*55*	$KMnO_4$(solid)	$^{55}Mn(n,\gamma)^{56}Mn$	Confirms Libby (1940)
Aten and van Berkum (1950)	*10*	$KMnO_4$(solid)	$^{55}Mn(n,\gamma)^{56}Mn$	Confirm Libby (1940) Retention rises to 70% if crystals heated to 180°C. for >20 mins.
Broda *et al.* (1950)	*20*	$KMnO_4$(solid)	$^{55}Mn(n,\gamma)^{56}Mn$	Retention increased by heating before dissolution
Rieder (1950) Broda and Rieder (1949)	*207* *20a*	$KMnO_4$(solid and soln.)	$^{55}Mn(n,\gamma)^{56}Mn$	Retention independent of velocity of activating neutrons
McCallum and Maddock (1953)	*146* –	$KMnO_4$ $NaMnO_4,3H_2O$ $Ca(MnO_4)_2,5H_2O$ $AgMnO_4$ $LiMnO_4,3H_2O$ $Ba(MnO_4)_2$ $LiMnO_4$ $NaMnO_4$ $Ca(MnO_4)_2$ (all solid)	$^{55}Mn(n,\gamma)^{56}Mn$	Confirm Libby (1940) Retention unchanged if $AgMnO_4$ pptd. instead of MnO_2: Ba^{++} increases retention at high pH

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TABLE X (continued)

Author and Date	Ref.	Compound	Reaction	Results*
Broda *et al.* (1950)	*20*	$KMnO_4$ solid soln. in $KClO_4$	$^{55}Mn(n,\gamma)^{56}Mn$	Results similar to those for pure $KMnO_4$
Fermi *et al.* (1934-5)	*66, 67*	$KMnO_4$(soln.)	$^{55}Mn(n,\gamma)^{56}Mn$	Recovery as MnO_2 by simply filtering irradiated solution through filter paper
Libby (1940)	*141*	$KMnO_4$(soln.)	$^{55}Mn(n,\gamma)^{56}Mn$	Retention small at pH 2-10, increasing at either extreme
Drehmann (1941)	*55*	$KMnO_4$(soln.)	$^{55}Mn(n,\gamma)^{56}Mn$	Confirms Libby (1940)
Broda *et al.* (1950)	*20*	$KMnO_4$(soln.)	$^{55}Mn(n,\gamma)^{56}Mn$	–
Jordan (1951)	*117*	$KMnO_4$(soln.)	$^{55}Mn(n,\gamma)^{56}Mn$	Results can be explained by production of Mn(II) or Mn(III) in recoils
Libby (1940)	*141*	$KMnO_4$ in acetone soln.	$^{55}Mn(n,\gamma)^{56}Mn$	Retention almost zero
Herr (1952)	*102a*	$KReO_4$ K_2ReCl_6	$^{185}Re(n,\gamma)^{186}Re$ $^{187}Re(n,\gamma)^{188}Re$ $^{185}Re(n,\gamma)^{186}Re$ $^{187}Re(n,\gamma)^{188}Re$	No separation: retention 100% in +7 state 30% as Re VII from solid 100% as Re VII from soln.
Croalto, Giacomello and Maddock (1952)	*37*	Na_2IrCl_6	$^{193}Ir(n,\gamma)^{194}Ir$ $^{191}Ir(n,\gamma)^{192}Ir$	Retention 37% Retention 47%

† See also Ref. *256*

* The 'products' mentioned in this column are the forms in which the activity was *recovered*. These are not necessarily the primary products of the nuclear reaction, which could equally well be any other forms exchanging readily with the carrier.

The total energy carried off by γ quanta in the (n,γ) reactions is about 8 MeV.;[141] it is distributed among 2-6 quanta emitted, apparently, without angular correlation.[283] The recoil energy of an atom of mass M which has emitted a quantum of energy $E\gamma$ (Me V.) is $(533/M)(E\gamma)^2$ electron volts.[141] This comes to an amount considerably, though not enormously, in excess of bond energies; e.g. manganese emitting a 2 MeV. quantum recoils with energy 40 electron volts.[141] Thus, bonds with the recoiling atom are broken without much discrimination.

In order that the isotope formed can be separated from the target substance by ordinary chemical operations in aqueous solutions, it is usually, though not always, necessary for it to be in a different oxidation state. This is most easily accomplished by irradiating a compound of the highest or next-to-highest oxidation state of the element (e.g. a chlorate or perchlorate for chlorine isotopes). Daudel has pointed out that the oxidation number finally taken up by the recoiling atom is zero or negative for electronegative elements (e.g. chlorine from ClO_4^- is recovered as Cl^-, and selenium from $SeO_4^=$ as the element) but may be positive for more electropositive ones (e.g. As(V) is converted to As(III) in the recoil, and Sb(V)· ends up as Sb(V), so that no separation can be effected).[211] Libby has expressed essentially the same idea in the rough rule that 'results of the recoils will correspond to distribution of the bonding electrons among the products about as they are distributed in the bonds broken'.[41] If a separation is to be possible, the chemical species formed must not undergo an exchange reaction with the starting material during dissolution in water or in the subsequent chemical treatment. This requirement is satisfied, except under special conditions, by the oxyacid anions, which do not exchange their central atoms so easily with other ions or atoms.

In some cases at least, separation can be effected either after irradiating the solid or after irradiating its aqueous solution.

More often than not, a considerable fraction of the radioactive atoms appears in the chemical form of the target substance instead of the altered form sought. This fraction, expressed as a percentage, is called the 'retention'. Much of the research in this field has been devoted to analysing the causes of 'retention'.[19,32,141,146] Among these are:-

(1) Failure of a proportion of recoils, owing to emission of several γ quanta simultaneously in such a way that their impulses largely cancel.[31,32,283]

(2) In some recoils, a collision between the recoiling atom and an adjacent anion, in which the former expels an atom of its own kind from the anion, and takes its place therein.

(3) When a solid salt is irradiated, there may be an exchange reaction between the product atoms and the target substance, brought about thermally or under the influence of ionizing radiation (which, almost inevitably, accompanies thermal neutrons).

(4) Exchange reactions occurring during chemical separation.

Nuclear Reactions Involving a Change of Atomic Number.

The examples of this type of reaction are listed in Table XI, with references and brief statements of the observations made. Most investigations have been

TABLE XI. - CHEMICAL FORMS OF PRODUCTS OF NUCLEAR REACTIONS IN SALTS OF THE ALKALI METALS (REACTIONS INVOLVING A CHANGE OF ATOMIC NUMBER)

Author and Date	Reference	Compound	Reaction	Results
Wilk (1949)	*282*	NaCl	$^{35}\text{Cl}(n,p)^{35}\text{S}$	^{35}S in a form exchanging rapidly with $SO_4^=$
Edwards and Davies (1948)	*62*	NaCl	$^{35}\text{Cl}(n,p)^{35}\text{S}$	Nearly all ^{35}S recovered as $SO_4^=$
Wilk (1949)	*282*	KCl	$^{35}\text{Cl}(n,p)^{35}\text{S}$	^{35}S in a form exchanging rapidly with $SO_4^=$
Croatto and Maddock (1949)	*35-37*	KCl	$^{35}\text{Cl}(n,p)^{35}\text{S}$	^{35}S recovered entirely as $SO_4^=$
Edwards and Davies (1948)	*62*	KCl	$^{35}\text{Cl}(n,p)^{35}\text{S}$	Nearly all ^{35}S recovered as $SO_4^=$
Koski (1949)	*131*	KCl	$^{35}\text{Cl}(n,p)^{35}\text{S}$	Up to 85% of ^{35}S recoverable as $S^=$ if crystals well outgassed
Koski (1949)	*130*	KCl	$^{35}\text{Cl}(n,p)^{35}\text{S}$	With outgassed crystals, ^{35}S appears as $S^=$ from interior and as $SO_4^=$ from outer layers
Milham (1952)	*166*	KCl	$^{35}\text{Cl}(n,p)^{35}\text{S}$	With vacuum-sublimed crystals, 90% ^{35}S as $S^=$ if dissolved in carrier solution directly. If dissolved in water, then carrier added, 30% as $S^=$, 70% as $SO_4^=$

TABLE XI (continued)

Author and Date	Reference	Compound	Reaction	Results
Croatto and Maddock (1949)	*35-37*	RbCl	$^{35}Cl(n,p)^{35}S$	50% of ^{35}S recovered as $S^=$, 50% as $SO_4^=$
Milham (1952)	*166*	RbCl	$^{35}Cl(n,p)^{35}S$	As found by Milham for KCl (see above)
Croatto and Maddock (1949)	*35-37*	CsCl	$^{35}Cl(n,p)^{35}S$	^{35}S recovered as $SO_4^=$
Kamen (1941)	*119*	RbCl	$^{37}Cl(d,\alpha)^{35}S$	95% of ^{35}S recovered as $S^=$
Caillat and Süe (1950)	*25*	LiCl	$^{35}Cl(n,\alpha)^{32}P$	^{32}P present initially about equally as P(v) and $P<(v)$. On heating to destroy colour centres, yield of $P<(v)$ increases relative to P(v)
Caillat and Süe (1950)	*25*	NaCl	$^{35}Cl(n,\alpha)^{32}P$	
Caillat and Süe (1950)	*25*	KCl	$^{35}Cl(n,\alpha)^{32}P$	
Aten (1942)	*9*	$Na_2SO_3, 7H_2O$	$^{32}S(n,p)^{32}P$	40% of ^{32}P as phosphite 60% of ^{32}P as phosphate
Aten (1942)	*9*	$Na_2SO_4, 10H_2O$	$^{32}S(n,p)^{32}P$	9% of ^{32}P as phosphite 91% of ^{32}P as phosphate
Whitmore (1949)	*279*	Na_2S	$^{32}S(n,p)^{32}P$	Nearly all ^{32}P as phosphate
Meier and Garner (1949)	*160*	Na_2SO_4 (anhydrons)	$^{34}S(p,n)^{34}Cl$	Essentially all Cl activity recovered as Cl^-
Meier and Garner (1949)	*160*	$K_2S_2O_8$	$^{34}S(p,n)^{34}Cl$	

concerned with the reaction $^{35}Cl(n,p)^{35}S$ in alkali chloride crystals. The ^{35}S atoms formed must lose their energy by collisions, and eventually lodge in interstitial sites in the lattice, where they would, for electrostatic reasons, settle down with no charge, or small negative or positive charges. On dissolving in water, active sulphide ions would be formed, or if not, active sulphur atoms or S^+ ions which would certainly undergo rapid exchange with sulphide carrier ions if these were present. One would therefore expect to be able to recover the ^{35}S as $S^=$ or H_2S by dissolving the irradiated alkali chloride in a solution of either of these carrier substances, and then separating the $S^=$ or H_2S. The results of studies of the chemical form of the ^{35}S are rather contradictory, but it seems that if the chlorides are painstakingly outgassed at high temperature in vacuo before irradiation, this expectation is realized. If they are not outgassed, all or much of the ^{35}S appears as $SO_4^=$, not $S^=$. Koski's experiments (see Table XI) suggest strongly that this is due to the presence of traces of oxygen in the crystals. Much $SO_4^=$ is also obtained if the carrier is not added until after dissolving the crystals in water - probably owing to the presence of a species such as S° or S^+, which would exchange with the carrier if this were present, but would otherwise be oxidized to $SO_4^=$ very quickly. The amount of hypochlorous acid resulting from dissolution of trapped holes (see page 2554) would more than suffice for this oxidation, since there is only about 10^{-9} g. of ^{35}S per g. of the alkali chloride.

The appearance of ^{32}P from the reaction $^{32}S(n,p)^{32}P$ in the form of $PO_4^{\equiv}$ can probably also be put down to the presence of oxygen in the sodium sulphide irradiated.

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SECTION CIII

THE USE OF RADIOACTIVE ISOTOPES OF THE ALKALI METALS IN BIOCHEMISTRY, PHYSIOLOGY AND MEDICINE

By W. C. HUTCHISON

The presence of all the alkali metals in biological materials has been reported, although lithium, rubidium and cæsium are classed as trace metals, and virtually nothing is known as to their function. Sodium and potassium on the other hand occur in relatively large amounts, and much research has been carried out on the part played by these elements in maintaining the special functions of living cells.

The only members of the alkali metal group which possess a naturally occurring radioisotope are potassium and rubidium which contain ^{40}K and ^{87}Rb to the extent of 0·012% and 27·2%, respectively. On disintegration ^{40}K yields calcium, and since potassium ions and calcium ions are known to be antagonistic in their action on the excitability of tissues, this change might be of interest biologically were it not so slow that its significance is doubtful. Speculation that the radioactivity of natural potassium is responsible for its biological function[1] is not supported by work[2] with isolated frog heart, which failed to produce evidence for the functioning of either ^{24}Na or ^{40}K in maintaining the normal heart beat. Similar conclusions have been reached in experiments with rubidium.[3]

It has been suggested[4] that the natural occurrence of ^{40}K supplies a convenient liquid standard of radioactivity. Such a standard, which can easily be prepared by making up a solution of analytically pure potassium carbonate, is very useful in the calibration and standardization of counters designed to deal with liquid samples, which are used extensively in the assay of radioactivity in biological materials.

The availability of radioisotopes of the alkali metals has increased both the amount of work carried out on the biology of these elements and the value of the results obtained. The conventional techniques of analytical chemistry as applied to the alkali metals are frequently laborious, and owing to the ubiquitous occurrence of these elements, determinations of minute amounts are often of doubtful significance. Results obtained by the classical methods therefore indicate only the grosser changes which occur, but by using radioisotopes a technique is available which greatly reduces the labour involved in the analyses and also makes it possible to study small changes in, for example, the distribution of substances on either side of the cell membrane.

The radioactive isotope of lithium, ^{8}Li, has a half-life of only 0·88 second, so that for practical purposes no radioisotope of this element is available for use as a tracer. Useful isotopes of all the other members of the group are, however, available. With sodium, work has been carried out using ^{22}Na and ^{24}Na, while for the other elements the most useful available isotopes are ^{42}K, ^{86}Rb, ^{131}Cs, ^{134}Cs and ^{137}Cs. The investigations made with the aid of these radioisotopes include absorption, distribution and excretion studies, studies of ion transport and membrane permeability, studies of circulation and blood flow, and clinical applications.

ABSORPTION, DISTRIBUTION AND EXCRETION

One of the earliest studies[5,6] of the distribution of the alkali metals involved the administration of salts of radiosodium and radiopotassium to human subjects. Sodium was rapidly absorbed from the gastro-intestinal tract, but potassium was absorbed much more slowly: in the first half hour 17% of the administered ^{42}KCl was absorbed compared with 58% of the ^{24}NaCl. On the other hand, another group of workers[7] found that in rats 90% of orally administered ^{42}KCl was absorbed after half an hour. The rate of absorption and excretion of sodium has also been studied using ^{24}Na.[8] The amount excreted was to some extent dependent on the size of the dose administered.

In some experiments the time taken for ingested radiosodium to appear in particular body secretions has been determined. For example, it has been found[9] that radiosodium can be detected in human milk within 20 minutes of intake, and that ^{24}Na appears in the pancreatic juice of dogs 3 minutes after intravenous injection.[10]

An interesting application of radiosodium is its use to test the enteric coating of capsules.[11] The capsules contain radioactive sodium chloride, and their passage through the digestive tract is followed by one counter, while a second counter held in the subject's hand is used to detect the appearance of the isotope in the blood consequent on the absorption. A consideration of the responses of both counters indicates where the capsule dissolves, and also whether it dissolves quickly or develops a small leak and allows the salt to escape slowly.

Bone contains quite a high proportion of sodium, there being on the average 1 molecule of sodium to about 30 molecules of calcium, excluding the sodium found in the extracellular fluid of the bone. Only about one quarter of this sodium is exchangeable, and though nothing is known of its metabolic significance, an attempt[12] has been made to follow the exchange of sodium in bone by means of an external counter placed over the patella. In this position about 50% of the counts arose from the radiosodium in the soft tissues covering the bone, but this was regarded as the best available site. The investigation was carried out using both ^{24}Na and ^{22}Na. The ratio of patella counts to serum specific activity showed considerable variation, ranging from 1·0 to 2·0 in 35 experiments. In the studies with ^{22}Na, it appeared that equilibrium of distribution was not obtained until 96 or more hours after injection. Bone also contains some potassium and it has been shown[13] that in the rabbit the activity of the bone potassium reaches about 25% of that of the plasma potassium 24 hours after administration. Experiments have also been carried out with teeth, and the incorporation of injected radiosodium into the enamel has been demonstrated.[14]

Plants contain considerable amounts of potassium, and many investigations have been carried out on the distribution of this element in various species of plants using ^{42}K. One interesting application of the isotope technique is found in work[15] on the uptake of ^{48}K^{82}Br by carrots. The amounts of the two isotopes present were estimated by taking counts at two different times and allowing for the different decay rates of the two isotopes. Experiments with plants have shown that the uptake of potassium should be regarded as comprising two quite distinct processes: on the one hand a non-metabolic uptake which is probably a simple exchange-diffusion process, on the other a metabolic uptake whereby the potassium is incorporated chemically into the metabolites utilized by the plant.[16-18]

A similar non-metabolic uptake has been demonstrated with rubidium using solutions as dilute as 10^{-9} M. The rubidium so absorbed is readily exchangeable, and the process, as with potassium, is for practical purposes independent of temperature, respiration rate and exposure to light.[18]

The route by which various ions are transported in plants has been studied[19] by separating the xylem or woody part from the bark by means of waxed paper and then showing that the upward movement of ions occurs entirely through the xylem. These experiments were carried out using radiosodium, radiopotassium and also radiobromine and radiophosphorus as phosphate. A similar technique has been used to show that the downward movement of phosphate ions, and so presumably of other ions also, occurs in the bark and not at all in the xylem.

For studies on the distribution of cæsium carried out by means of radioisotopes one must turn to marine plants. Marine algæ normally concentrate potassium in preference to sodium, in spite of the fact that sea water contains a very high concentration of the latter. There is some evidence that they will show an even greater preference for the higher members of the alkali metal group and, because cæsium occurs in reasonable amounts in nuclear fission products, it is of some biological importance to determine the extent of the incorporation of this material into marine algæ. Using $^{134}Cs_2SO_4$, the uptake of cæsium by various species of marine algæ has been investigated.[20] The normal incorporation of cæsium appeared to depend on the incidence of light and the presence of carbon dioxide, while it was enhanced in sea-water in which the potassium had been replaced by sodium. In the last case the plant is presumably endeavouring to compensate for the deficiency of potassium by increasing its absorption of cæsium.

ION TRANSPORT AND CELL PERMEABILITY

The living organism is composed of a number of different phases – gases, liquids, gels and solids – and the boundaries where different phases adjoin have very special and interesting properties. The conditions may be simply those associated with the semipermeable membrane, or there may be active secretion and transport of substances across the boundary. Often these boundaries are associated with actual membranes, and this is usually so at the periphery of the cell or of a particular structure within the cell such as the cell nucleus. It is probably incorrect, however, to think of the cell membrane, for example, as being the boundary between two different phases, for there is some evidence that the cell membrane is composed of lipid-like material so that between the contents of the cell on the one hand and the extracellular fluid on the other there are two interfaces of the fat/water type. Many of these membranes have remarkably selective properties with regard to metabolites, and probably the best known example is to be found in the segregation of sodium and potassium in blood. The red blood cell of most mammals is able to maintain a high internal concentration of potassium ions in the presence of a low concentration in the plasma; and at the same time to exclude to a large extent ions of sodium, even though the concentration of these ions in the plasma is quite high. All this, of course, indicates that ion-transport is governed by some active mechanism, and not merely by the rules of simple diffusion.

Many attempts have been made to determine the nature of this mechanism without producing a theory which was acceptable universally. However, the availability of radioisotopes, especially those of the alkali metals sodium and potassium, has made the study of the problem much simpler, and has produced much new information.

Excluding experiments on erythrocytes or red blood cells, relatively few experiments have been carried out on the penetration of the alkali metal ions into single cells. It has been reported[21] that the bacterium, *Escherichia coli*, is freely permeable to potassium ions. Studies on the exchange of sodium in the frog egg have shown[22] that only 12% of the sodium present is readily exchangeable; this fraction comes into rapid equilibrium with the sodium of the medium, but the remaining 90% may take as much as 10 hours to equilibrate.

Yeast has also been the subject of several investigations. Using ^{42}K it was found[23] that in actively fermenting yeast the interchange of potassium between the yeast and the nutrient solution was almost complete in the course of 2 hours, whilst there was relatively little exchange of potassium with yeast which showed only slight fermentative activity. It is believed that in those experiments where marked exchange occurred, the actual amount of potassium exchanging was probably even greater than that detected, since, as the exchange proceeds, the ^{42}K in the nutrient solution available for exchange is diluted by non-radioactive potassium originally present in the yeast. In connexion with these results it is of interest to note that, using purely chemical methods, it has been found[24] that the membrane of yeast cells becomes more permeable during the fermentation process. The influence of *X*-rays on the permeability of yeast to potassium has been studied,[25] since it has been suggested by several workers that at least a partial explanation of the effect of *X*-rays on tissues might be that it produces changes in the permeability of the cell. Such a change could influence the entry into the cell of substances concerned in the process of cell division, and the elimination of excretory products from the cell might also be affected. It is inadvisable to study the effect of *X*-rays on the permeability of yeast by determining the amount of potassium penetrating into the yeast cell before and after irradiation. The growing yeast cell takes up substances essential for its metabolic processes, and a diminution in uptake of such substances after irradiation cannot be interpreted as necessarily due to changes in permeability of the cell membrane. Accordingly the method used[25] was to grow the yeast in the presence of ^{42}K in the medium, thus producing ^{42}K-labelled yeast. This labelled yeast was then shaken with non-radioactive nutrient solution and the rate at which the radiopotassium appeared in the nutrient solution was determined. Similarly other batches of labelled yeast were irradiated prior to shaking with the non-radioactive medium, and differences in the rates at which the ^{42}K appeared in the medium in the two cases were interpreted as differences in cell permeability. The effect of the *X*-irradiation on the permeability was relatively slight, a dose of 30,000 roentgens, which killed 90% of the yeast cells, causing an increase in permeability of only 30%. Ultra-violet radiation has no effect on the permeability of yeast cells to potassium, but the presence of arsenate cuts the amount of potassium migrating from the cells to about 50% of the normal value.

In the field of plant physiology, a study has been made of the permeability of *Nitella* to sodium and potassium chlorides.[26,27] Cells of *Nitella* labelled with either ^{24}NaCl or ^{42}KCl were placed in solutions of the chlorides of the other alkali metals. Using sodium, the most rapid loss occurred when the cells were placed in solutions of lithium chloride, and the least rapid loss in solutions of cæsium chloride. With potassium, the loss followed the Hofmeister series, the slowest rate being observed with lithium chloride solutions. Little or no loss occurred when the cells were placed in distilled water.

Many aquatic animals have the ability to take up certain ions such as sodium and chloride ions from the surrounding medium. This uptake may occur through the gills, as in the fish, or it may occur through the whole surface of the animal, as in the frog. The ions may be taken up from a solution as dilute as 0·01 millimolar and the concentration of salt thus effected may be as much as 10,000-fold. In a study of the penetration of the radioisotopes of sodium and rubidium through the excised skin of the frog,[28] the inner surface of the skin was placed in contact with an isotonic solution of the salt and the rate of appearance of the isotope in the distilled water bathing the outer surface of the skin was studied over a 2 hr. period. Sodium chloride was found to pass through the skin at the rate of $4{\cdot}7 \times 10^{-12}$ mole per sq. cm. per sec., while rubidium chloride penetrated more rapidly at the rate of 125×10^{-12} mole per sq. cm. per sec.

The significance of these observations must be assessed in conjunction with the results obtained[29] in very similar experiments in which the inner surface of the frog skin was bathed with Ringer's solution, and the outer surface with extremely dilute solutions of dissolved salts. With this arrangement, it was possible to show an active movement of radiosodium ions from the outside of the skin to the inside even though the concentration on the outside was as low as 1 milliequivalent per litre.

The uptake of sodium and chloride from the surrounding medium has been studied with the aid of ^{24}Na and ^{38}Cl in the case of the adult axolotl (*Amblystoma mexicanum*).[30,31] The animals were maintained in solutions of ^{24}Na^{38}Cl having concentrations ranging from 0·001 to 0·003 N. The concentration of sodium and chloride ions in the axolotl's blood is about 0·1 N., so that the radioisotope taken up will be a measure of the 'active intake', the amount taken up by diffusion processes being considered negligible. The concentration of radioisotopes in the solution was not allowed to fall below 50%, and it was thus permissible to neglect losses of radiosodium from the animal, by, for example, urinary excretion. Averaging the results of several experiments, it was found that in the normal animal the amount of sodium taken up in 24 hr. was approximately equal to the amount excreted, being about 0·08 milliequivalents in each case. Injection of a hypophyseal extract, insipidin, caused a 200% increase in uptake of sodium and a 95% increase in the sodium excreted. On the other hand a preparation containing oxytocin produced an increase in the amount of sodium excreted without affecting the sodium uptake. The net loss of sodium and chlorine was maintained for several days. It might be expected that injection of sodium chloride solution into the blood stream of the animal would affect the uptake of this substance from the surrounding medium; yet it was found that the injection of 1 ml. of 4% sodium chloride caused no significant alteration in the normal picture, and the axolotl could continue to take up sodium and chlorine after the injection.

In higher animals having a circulatory blood system containing corpuscles, there are several possibilities of exchange. Ions in the blood plasma may pass through the capillary wall into the extracellular fluid of the tissues or into the tissue cells. Alternatively, without leaving the blood stream, the plasma ions may pass through the erythrocyte membrane and so enter the red blood cell. The various members of the alkali metal group exhibit different properties depending on the routes by which they leave the plasma.

Considering first the passage of substances from the capillary into the extracellular fluid, the rate at which different substances will reach equilibrium will depend on whether the substance under consideration occurs in the body in the extracellular fluid alone, in the tissue cells alone, or in both sites. Reference has already been made to the different rates at which sodium and potassium come into equilibrium: this is due to the fact that sodium is largely extracellular in its distribution, though it is present within the cells of certain tissues, while potassium is largely an intracellular element. The process of equilibration is therefore, for sodium, relatively simple, since the sodium – once it has found its way into the blood – has merely to pass through the capillary walls to mix readily and rapidly with the extracellular fluid. A small amount of the sodium, it is true, must be taken up by the bone, the red blood cells, and the muscle, but the amount concerned is so small as to have little influence on the final result. The situation with regard to potassium is more complex, because of the very significant amount of potassium that will penetrate the tissue cells. The amount of potassium entering the cells of the body can be calculated to be about fifty times the amount entering the extracellular fluid. The relative rates of disappearance of different ions have been calculated by measuring the rate of disappearance of a variety of different radioactive ions from the blood plasma to the cerebrospinal fluid.[32] The technique was to remove the cerebrospinal fluid from large dogs, inject the radioisotope, and compare the activities of the isotope in the plasma and in the freshly secreted cerebrospinal fluid. It seems certain that under the conditions of the experiment the rate of formation of the cerebrospinal fluid was much higher than normal, so that the rate of transference of ions from the blood to the cerebrospinal fluid may also have been exaggerated. Even so, the relative rates of disappearance could well have been normal. These were for the members of the alkali metal group studied $K = Rb > Na$. Other workers, however, have pointed out[33] that the injected radioactive ions, and the ions already present in the plasma, will leave the plasma at the same rate, and since the concentration of sodium in the plasma is about twenty times that of the potassium, it may be assumed that the amount of sodium leaving the plasma per unit time will be appreciably higher than the amount of potassium.

Although the general method of studying ion transport involves the study of the appearance or disappearance of a radioactive tracer on one side of a membrane or phase boundary, it must not be forgotten that the final equilibrium reached in the living organism is a dynamic equilibrium in which the particular ions may well be, and probably usually are, travelling across the membrane or phase boundary in both directions at the same time. Thus, from a study of the transference of sodium from the plasma to the extracellular fluid in guinea pigs[34] it was calculated that the amount of sodium transferred per minute in either direction across the capillary wall was equal in amount to 60% of the plasma sodium or 13% of the sodium in the extracellular fluid.

The determination of the volume of the extracellular fluid is of considerable interest to workers in the fields of biochemistry, physiology and clinical medicine, and several methods have been devised to measure this quantity. What is required is a non-toxic substance which will distribute itself rapidly and exclusively throughout this phase, will not itself be metabolized, and will be excreted only slowly. Using classical analytical techniques, the substance which approaches this ideal most closely is thiocyanate. However, it is well known that anions penetrate only very slowly into the cerebrospinal fluid and the extracellular space in brain and nervous tissue, and thiocyanate is no exception. The availability of radioactive cations such as $^{24}Na^+$ seemed to hold out the possibility of overcoming this objection. However, as will be discussed below, it became apparent that the blood–brain barrier applied to sodium ions as well as to anions, and in addition a somewhat uncertain correction must be applied to allow for the equilibration of the plasma sodium with the bone sodium. This being so, the isotopic technique has few advantages over the classical technique, but several studies have nevertheless been made of the extracellular space of the body using radiosodium.

Such determinations[35,36] have shown that the entrance of sodium into the extracellular space of nervous tissue was much delayed. Thus, after a period of 2 hr., values of only 14·9% and 10·9% were found for the extracellular space of the grey and white matter of the brain, though after a period of 62 hr., from the administration of $^{24}NaCl$, a value of 31% was obtained for the whole brain which approximates to the accepted value. The more rapid uptake of sodium by the grey matter is possibly due to its greater vascularity. As a result of the examination of a large number of tissues it appears that these can be divided into two groups.[35] The first group, including skin, kidney, liver and probably also heart, gastro-intestinal tract, abdominal muscle and gastrocnemius muscle, represents tissues into which the radiosodium penetrates completely in 20 minutes and remains constant for at least 12 hr. The second group comprises tissues into which the radiosodium penetrates slowly and may take as much as 12 hr. to attain equilibrium. The inclusion of muscle tissue in the first group is rather problematical. There is good evidence that the entry of the sodium into the gastrocnemius muscle may be complex. The evidence points to the entry of the radiosodium into part of the extracellular space within 20 min., this part corresponding to the chloride space, determined using chloride ions. More time is apparently required to penetrate the whole sodium space in muscle. In view of the low level of intracellular sodium in muscle it is very difficult to determine the rate at which this substance is replaced. It may be noted, however, that rats have been reared on a potassium-deficient diet, when the muscle potassium is replaced to a considerable extent by sodium,[37] and that in such muscle it took 1 hr. to attain equilibrium between the cellular sodium and the administered ^{24}Na.

Attempts have been made to determine the sodium space of rats by using ^{22}Na as the tracer.[38] In these experiments two groups of rats were fed respectively on a normal diet and on one deficient in chloride but containing excess of carbonate and bicarbonate. The animals fed on the low chloride diet had a sodium space about 25% greater than that of the control animals. In another investigation using ^{22}Na, it was found that it might take as much as 96 hr. before equilibrium was attained in bone.[12]

It seems therefore that when radiosodium is injected it passes fairly rapidly into an extracellular space which represents about 25% of the body weight in man, and then more slowly into the skeleton and also into the nervous system. There is also some slight penetration into the red blood corpuscles which will be discussed below. For the present purpose it is sufficient to note that the correction involved is very small, except for the dog and the cat which have a relatively large amount of sodium in their red blood cells. In the skeleton, it appears that the sodium ions replace the calcium in the surface layers of the bone apatite, and only about a quarter to a third of the bone sodium is indeed extracellular. The discovery of the slow rate of equilibration with the cerebrospinal fluid and the nervous system, attributed to the so-called blood-brain barrier, was the first indication that this barrier could apply to one of the physiologically important cations. Experiments by the classical methods had demonstrated the existence of this barrier for anions, and the evidence suggested that anions reached the cerebrospinal fluid by a process of secretion. That a similar mechanism may apply to some cations has been suggested by the work already mentioned[32] which involved draining off the cerebrospinal fluid from dogs, and studying the rate of appearance of radioactive ions from the blood plasma in the revewed cerebrospinal fluid. Potassium showed the highest rate of penetration, and the other ions followed the series K>Na>Br>Rb>Sr>P>I. When radioactive potassium, rubidium and phosphorus were injected into the blood stream, the radioactivity of the cerebrospinal fluid showed maxima at approximately 20, 30 and 60 minutes respectively, and this was interpreted as indicating a secretory mechanism of transfer. Radiosodium showed no maximum. Studies have also been made[39] of the equilibration between sodium chloride in plasma and in cerebrospinal fluid using ^{24}Na, and in the technique employed the disturbance to the cerebrospinal fluid was less than in the work just described. At intervals small samples were taken simultaneously from the plasma, the lateral ventricles, the cisterna magna and the lumbar subarachnoid space. The results indicated that the fluid in the cisterna magna came into equilibrium with that in the ventricles within 1 hr. but that it took about 4 hr. to attain equilibrium in the subarachnoid space. These findings have been confirmed[40] by another group which has recently[41] reported an extended study of the subject with the inclusion of human pathological material.

It has been shown by several groups of workers (e.g. [42]) that by comparing the amount of ^{24}Na injected into the plasma with the amount remaining after a period of time, it is possible to calculate the total volume of fluid available to dilute the injected isotope. This is the total extracellular fluid of the organism and for most animals it has been found to vary between 23% and 29% of the body weight. It is interesting to remark that if a similar experiment be made using radiopotassium it gives a figure, after only 5 minutes, of 70% of the body weight, when the corresponding figure for sodium would be only 15%. After longer periods of time the difference is even greater, and the result points clearly to the intracellular penetration of potassium.[36]

In addition to studies of the penetration of ions through the walls of the blood capillaries, investigations have been made of the permeability of several other regions of the body. Thus, the penetration of the intestinal wall by ^{24}Na has been studied.[43] Normal considerations of concentration gradients, diffusion and osmotic effects fail to account for the amount of sodium taken up by the intestinal wall. Also, as the movement of ions in both directions was studied and not merely the net change in concentration on one side of the intestinal wall, it was possible to show that sodium is constantly passing from the blood plasma into the lumen of the intestine even while active absorption of sodium into the plasma is taking place. The authors found, incidentally, that an amount of sodium equal to the total amount of sodium in the blood plasma is exchanged between the intestine and the blood in a period of 83 min. A similar study of the transfer of sodium and potassium across the bladder and colon has recently been made,[44] and led to similar conclusions regarding the dynamic nature of the equilibrium.

Absorption from the stomach has been studied by other investigators[45] who found that absorption from the pyloric antrum was considerably greater than from the body of the stomach, in some cases as much as 100 times as great. The absorption of sodium and potassium was much slower than that of chloride.

The permeability of the placenta has been studied using a number of different species.[46] Radiosodium was injected into the animal, and after a period of time the radioactivity of the maternal blood was compared with that of the foetus. The rate at which the foetal sodium equilibrates with the maternal plasma sodium was found to be quite slow. In the rat it took 6 hr. and in the cat 12 to 18 hr. to reach 90% equilibrium. This is in striking contrast with the fact that after injection of radiosodium, 90% equilibrium between the plasma and the maternal extracellular fluid is reached in 4 to 5 min. As gestation proceeds and the placenta increases in weight there is an increase in the rate of transfer per unit weight of placenta. Thus, in the rat in the last week of pregnancy, the rate of transfer of sodium across the placenta increases 6 times. In this period the amount of sodium transferred is some 27 times as much as is incorporated in the growing tissues. The transfer rate decreased sharply just before term, and over the whole period of gestation the placenta transfers about 25 times as much sodium as is present in the foetus at birth. As with other species, in the human placenta the rate of transfer of sodium increases during the course of gestation. At 10 weeks the rate of sodium transfer was 0·76 mg. per g. of placenta per hr., while at 37 weeks the rate had increased some 6-fold.[47] It has been claimed that the results show that the rate of transfer of sodium across the placenta depends on the number of layers of cells between the maternal and foetal circulations and that it can also be correlated with the rate at which the unit weight of foetus was growing.[46] It is interesting to compare the behaviour of sodium with that of phosphorus: during the gestation period the amount of phosphorus transferred across the placenta is only very slightly more than that present in the foetus at term.[47] The same group of workers has studied the production of the amniotic fluid.[48] The turnover time of the water in the amniotic fluid is about 1 hr. and it has been shown, using radiosodium, that the rate of transfer of sodium is much slower than this, being, in the guinea pig, about one fiftieth of the rate of water transfer at various stages of gestation.

The absorption of radiosodium from the vagina has also been investigated, but the results show an extremely wide variation.[49]

The aqueous humour of the eye is regarded as a secretion produced in a similar fashion to the cerebrospinal fluid, and the rate of appearance of radiosodium in the aqueous humour after injection of the isotope into the blood has been studied. It was found[50] that the activity in the aqueous humour reached 50% of that in the plasma after 40 min., while a level of 75% of that in the plasma was found after 45 min.[51] It was estimated that the rate of equilibration between the plasma and the aqueous humour was some 2 to 4 times the rate of equilibration between the plasma and the cerebrospinal fluid in the cisterna magna. A proof that the sodium enters the aqueous humour by secretion is afforded by the results of experiments in which radiosodium was administered intraperitoneally to rabbits which had one common carotid artery blocked.[52] In samples of the aqueous humour taken from both eyes 40 to 60 min. afterwards, no difference was found in the amount of radiosodium. This would not have been expected had the sodium reached the aqueous humour by a process of diffusion or ultrafiltration, since the occlusion of the common carotid artery is accompanied by a marked decrease in blood pressure in the arteries supplying the eye on the same side, and the drop in pressure would be followed by a drop in the rate of diffusion or filtration of sodium into the aqueous humour. Since this was not observed, it is concluded that the sodium enters the aqueous humour by a process of secretion.

As has already been mentioned, potassium is to be regarded mainly as an intracellular element, and many experiments have been carried out to study the partition of potassium between the blood plasma and the tissue cells. Muscle cells contain considerable amounts of potassium, and the penetration of this element into the cells of muscle tissue has been the subject of many investigations. In some of these studies, radiopotassium was administered to the experimental animal, and measurements were carried out of the radioactivity of 1 g. of plasma and of 1 g. of muscle. A comparison of the two figures, taking into consideration the extracellular volume of the muscle and also the potassium concentration in muscle and in plasma, enables a calculation to be made of the partition of potassium between the plasma and the muscle cells. The results of such an experiment show quite clearly that the ^{42}K ions penetrate the muscle cells rapidly, but the data obtained are not sufficient to allow the calculation of exchange rates, for which a knowledge of the specific activities of the plasma potassium and the intracellular potassium of the muscle is also required.

An exhaustive series of investigations of the exchange rate of plasma potassium and the potassium of several organs has been carried out[13,53] using rats, rabbits, guinea pigs and frogs. The results demonstrate that all the potassium in the body is exchangeable, and hence that the cell membranes of all the tissues of the body are permeable to potassium ions. However, marked differences were found when the various organs were compared. In the liver, kidney, heart, diaphragm, lung and skin, the specific activity of the tissue potassium reached a value greater than that of the plasma potassium, although in the skin this state was not reached for some 20 hr. after injection of the ^{42}KCl. These results must indicate an active removal of the potassium from the plasma by the tissue, and not a simple exchange process. The amount of ^{42}K which had to be administered to the animals in order to produce an adequately high level of radioactivity for accurate determination was an appreciable porportion of the normal amount of potassium circulating in the plasma. The amounts used ranged from 0·3 to 2 milliequivalents per kg. body weight, so it must be assumed that the administration of the radioactive potassium chloride so raised the plasma potassium in the initial stages of the experiments that the body reacted by active removal of the excess potassium by various organs. Such data cannot therefore be regarded as giving a good indication of the rate of exchange in different tissues, though it should be noted that only the tissues mentioned showed a specific activity higher than that of the plasma potassium. Other tissues, such as muscle, brain, bone and testis showed a much lower rate of exchange. Different animals also showed different rates of exchange for the same tissue.

It should perhaps be noted here that much of the work carried out on potassium exchange at this time made use of ^{42}K obtained by cyclotron bombardment. There is therefore a possibility that the radiopotassium may have been contaminated with ^{24}Na, and since sodium is generally to be regarded as an extracellular element, this impurity would tend to indicate a lower rate of exchange than had actually occurred. In the work just mentioned, the authors consider that this is the explanation of some lower exchange rates previously reported (e.g. [54]). Although they themselves used cyclotron-produced ^{42}K, they took the precaution of precipitating the potassium as the perchlorate after the bombardment to get rid of any traces of radiosodium.

A study was also made[13,53] of the rate of total interchange of potassium in the body, that is the extent to which interchange of all the potassium in the body takes place in the course of one day. With animals this was carried out by dissolving the whole body of the animal and comparing the specific activity of the whole body potassium with that of the plasma. The results indicated complete interchange within 1 day in the cat, rat and guinea pig, but in the rabbit only about half of the body potassium appeared to be exchanged in this period. The other half of the body potassium appeared not to exchange at all or to exchange at a very slow rate indeed. A similar result was obtained with human subjects. These drank the radioactive potassium chloride as a solution, and the specific activity of the urinary potassium was then determined, since this was found to be approximately the same as that of the plasma potassium. Assuming that the overall concentration of potassium in the human body was of the same order as that determined in the animals analysed, it was calculated that about half of the total body potassium exchanged in one day.

It is difficult to accept these figures for the rabbit in view of the finding by the same workers[53] that complete exchange takes place between the plasma potassium and the muscle potassium in the rabbit, and the fact that about two thirds of the total body potassium occurs in the muscles. In addition it is noteworthy that it has been calculated from the potassium content and radioactivity of the urine in the human experiments that a very large proportion of the body potassium exchanges in the course of a single day.[55]

The effect of severe exercise on the exchange of potassium in rat muscle has been studied,[56] and also the effect of stimulation of the muscle on the exchange rate.[57] Both groups found a marked increase in the uptake of potassium in the experimental animals as compared with the controls. Thus, the first group found an average of 4·2 times as much ^{42}K penetrating the muscles of the rats forced to do severe exercise as entered the muscles of the resting animals. The second group, who investigated separately individual muscles in the rats, found an increase of 3·6 times in potassium uptake in the stimulated muscles. During exercise there is an increase in the blood flow to the active muscle, and the authors attempted to explain their results on the basis of this increased circulation rather than as a result of increased permeability. It seems more likely, however, that an increase in the rate of interchange between the intracellular and extracellular potassium is the true explanation.

Denervation was also shown to effect an increased penetration of potassium into muscles, and an apparent doubling of ^{42}K uptake by rat muscles was obtained under these conditions. Similar results have also been obtained in experiments[58] which showed that denervation of the gastrocnemius muscle of rats produced an increased penetration of radiopotassium 2 to 9 min. after injection of the isotope. Such denervated muscle took up to 2·8 times as much ^{42}K as did the controls.

An estimation of the actual amount of potassium crossing the cell wall has been made with the aid of radiopotassium[59] using chick embryo muscle cultures. The rate of penetration of potassium into the cell was found to be $14{\cdot}0 \times 10^{-7}$ millimole per sq. cm. per hr. The figure obtained for phosphorus penetration was much lower, $1{\cdot}57 \times 10^{-7}$ millimole per sq. cm. per hr.

Potassium ions have for some time been regarded as being concerned in the normal functioning of nervous tissue and, in particular, some evidence has been presented that they may be concerned in the transmission of nerve impulses. Radioactive potassium has been utilized in the study of this subject.[60-62] It appears that when a nerve impulse passes along a nerve K^+ ions are released, and Na^+ ions which are normally outside the axon, or nerve fibre proper, enter the fibre to replace the potassium. When the nerve is stimulated the rates of passage of potassium outwards and of sodium inwards are both increased, so that the net result is a tendency for the replacement of potassium by sodium in the nerve fibre. It has also been demonstrated that eserine and di-*iso*propyl fluorophosphonate, both of which are inhibitors of choline esterase (the enzyme that hydrolyzes acetylcholine which is also implicated in nervous transmission), increase the permeability of the nerve to sodium, but in these cases the permeability to potassium is diminished.

The investigations dealing with cell permeability already discussed illustrate problems which it would have been almost impossible to attack without the aid of radioactive isotopes as tracers. The classical methods of analysis would be incapable of detecting the small amounts of material transferred across cell membranes and, in addition, the organization of cells into the so-called fixed tissues of the body introduces further difficulties. The only instance where the study of cell permeability using the classical approach yielded useful results was that of the red blood cell, which is, of course, not a fixed cell, but floating free in the plasma. Even so, the amounts of substances used in such studies were frequently unphysiological, and the isotopic method has therefore been applied also to the study of ion penetration into the red blood cell. Among the animals used, the cat and dog are exceptional in having red blood corpuscles with a high sodium content, the potassium content being correspondingly diminished.

The permeability of the red cell to potassium has been investigated by different groups of workers.[63,64] The earlier results[63] are not regarded as giving a true picture of the partition of potassium between the plasma and the erythrocyte because of the possible presence of ^{24}Na in the potassium used. In later experiments,[64] in which the potassium was purified from possible sodium contamination before use, variable results were obtained for the exchange of plasma potassium and the erythrocyte potassium according to the species studied. In the cat, where the red blood cells contain some 17½ times as much sodium as potassium, complete interchange of the plasma potassium and cellular potassium occurred in the course of 15 hr. In the rabbit about 50% exchange was observed in the course of 1 day, while in the frog about 20% exchange occurred in about 10 hr., but thereafter no further interchange was observed. Such a result is extremely difficult to understand and no satisfactory explanation can be offered. In man, the degree of penetration amounted to about 40% in 10 hr. More recently, the exchange rate of red cell potassium has been reinvestigated[65,66] using human erythrocytes *in vitro*. The ^{42}K was not cyclotron-produced, but was obtained from the nuclear reactor, and can be considered as being absolutely free from contamination with ^{24}Na. In this way it was found that the exchange rate of potassium was from 1·6 to 1·8% per hr. with a temperature coefficient (Q_{10}) of 2·2. It is noteworthy that this temperature coefficient is identical with that obtained for glucose utilization by the same cells. It was also found that all the potassium in the cell is exchangeable with that in the plasma, and that the rate of exchange is independent of the state of oxidation of the hæmoglobin in the cell.

It must be remembered that the results of such experiments as have already been described give a measure of the rate of exchange of potassium between the red blood cell and the plasma. They do not give any information about the amount of potassium which will enter the red blood cell as a result of, for example, a raised level of potassium in the plasma. In such an investigation[67] only small changes in the exchange rate of red cell potassium were obtained with varying concentrations of potassium in the plasma. The net amount of potassium that entered the cell was negligible, even though the plasma-potassium concentration was raised to values which were 4 to 15 times the normal. While exchange of potassium does take place, the entry into the cell of any excess potassium must be compensated by the loss from the cell of some other cation, such as sodium, which is normally present in the cell in small amounts. The evidence suggests that such exchange takes place only to a limited extent.

In the dog, whose red blood corpuscles contain only about one-tenth of the amount of potassium in human erythrocytes, it is found that excess potassium in the plasma penetrates into the red cells easily. The potassium content of the corpuscles is doubled in about 2 hr. by an increase in the plasma potassium of 8 times.[68]

Some experiments[69] have indicated that the rate of penetration of plasma potassium into the red blood cell is increased by bee venom. The same author has also investigated[70] the penetration of ^{42}K from labelled red cells into unlabelled plasma, and has found that in a period of 2 hr. about 5% of the radiopotassium in the cells moves out into the plasma.

With regard to sodium penetration into red blood corpuscles, mention should be made of work on the penetration of ^{24}Na into the red cells of the dog both *in vivo* and *in vitro*.[71] It was found that half the cell sodium exchanged with the plasma sodium in a period of about 17 hr. In the cat, which like the dog has a high corpuscular sodium content, the rate of exchange may be slightly more rapid, 10 to 15% of the cell sodium being replaced in 1 hr.[64,72] Early experiments using rabbits, where the sodium content of the red cell is small, indicated that all the erythrocyte sodium was replaced by the plasma sodium within 24 hr.[63]

The fact that the concentration of potassium inside the red blood corpuscles of most species is higher than that in the plasma and the observation that an increase in the plasma potassium concentration fails to bring about a significant increase in the intracellular concentration of this element, are consistent with the classical view that the membrane of the erythrocyte is impermeable to potassium. However, from radioisotope studies it is clear that this is by no means true, and it is necessary therefore to consider how a membrane which is permeable to both sodium and potassium ions, can, in effect, partially segregate these ions, so that in most cases the bulk of the potassium is maintained inside the cell, while the bulk of the sodium is extracellular. This problem is, of course, not confined solely to erythrocytes, since in the fixed tissues as well, potassium and sodium are respectively intracellular and extracellular elements. This distribution of sodium and potassium cannot be explained in terms of the Gibbs–Donnan law, although this supplies a satisfactory explanation of the distribution of anions on either side of the cell membrane.

The high potassium concentration inside the red blood corpuscle and the osmotic pressure of the plasma make it difficult to envisage the cellular potassium as existing in the form of free potassium ions. If, however, the potassium is imagined as existing inside the cell in the form of a chemical compound and if it is assumed that this is a chemical combination into which sodium cannot enter, it becomes possible to explain the partition of sodium and potassium by the cell membrane on the basis of their relative chemical affinities for substances within the cell.

As a result of studies of the permeability of cell membranes it has been suggested[73] that the difference in chemical affinity operates in the membrane itself. The membrane is visualized as resembling a model, already postulated for plant cells, in which the boundary layer of the cell contains micelles which have definite affinities at each end, in a similar fashion to the molecules in a Langmuir film. If it is postulated that in the erythrocyte, for example, these micelles can bind specifically sodium and potassium ions at different ends, then, if the micelles are all similarly oriented, an effective partition of the two elements will be achieved. However, just as in the Langmuir film, a single micelle will occasionally turn, and ions normally present on the inside of the cell membrane will be presented on the outside, and may be split off. At the same time the ion normally extracellular will be accepted inside the cell.

Though this theory is ingenious, it seems much more probable that the intracellular binding of potassium is concerned with its function as a specific activator for certain enzymes concerned in the metabolic processes going on inside the cell, notably those concerned with the metabolism of carbohydrate. It is known, for example, that potassium exerts such an effect on the enzymes fructokinase and ATP-pyruvic transphosphorylase. There is a considerable amount of experimental evidence in favour of the participation of potassium in the reactions used to metabolize carbohydrate. Thus, it has been shown[74] that the utilization of glucose by the rat diaphragm muscle is accompanied by the simultaneous movement of potassium from the medium into the muscle. The maintenance of a high potassium and a low sodium level in the cells of nervous tissue such as brain cortex has been shown to depend on the maintenance of active carbohydrate metabolism in these cells. Similarly, loss of potassium from red blood cells occurs when the processes of carbohydrate metabolism are inhibited. Storage of human blood at temperatures of 2–5°C. for some time causes a leakage of the intracellular potassium, but when the temperature of the blood is raised the original distribution of potassium is largely restored. Corpuscles which continue to carry on the metabolism of glucose maintain their potassium content longer than those in which the supply of glucose is depleted. Thus, blood stored at 2–5°C. with glucose loses less potassium than blood stored under the same conditions without glucose.[73,75,76] It has been shown that brain cortex slices will, in the presence of glucose, absorb potassium ions and also glutamic acid. Similarly, in studies of the retina, the uptake of potassium requires the presence of glutamic acid in the nutrient solution. Since the amounts of potassium and glutamic acid taken up are approximately equivalent, it has been suggested that the cationic potassium ions 'partner' the anionic glutamate ions in the process of absorption. It appears that this ability of glutamic acid to aid in the transport of potassium ions across the cell membrane is highly specific. Other amino acids will not replace glutamic acid, and even glutamine is ineffective.[77-79]

While the detailed steps of the process of absorption are not known, it seems clear from the evidence that the segregation of potassium and sodium on either side of the cell membrane is connected in some way with the functioning of these elements in metabolic processes, since potassium aids reactions carried out inside the cell – reactions which have been shown in some cases to be inhibited to some extent by sodium. It is worth noting, however, that the active transport of the two substances appears to involve different mechanisms since in some cases lithium will interfere with the absorption of sodium but not of potassium, while rubidium will compete with potassium but not with sodium.

Some of the investigations carried out on the transfer of ions across cell membranes have been the subject of reviews.[80,81]

It is well known that the suprarenal glands have a powerful influence on the electrolyte balance of the body, the effect being particularly concerned with the distribution of sodium and potassium. It is not clear exactly how the adrenal hormones responsible act, but it may be that their action is a specific one on kidney cells, and that by altering the amount of sodium and potassium excreted changes in the distribution in the body as a whole are evoked as a compensatory mechanism.

STUDIES OF CIRCULATION AND BLOOD FLOW

The classical methods of studying the rate at which the blood flows through the body depend on the introduction into the blood stream of some substance which will produce a recognizable response at some site distant from the point of injection. Among the substances that have been used in this way are dyestuffs, saccharin, which produces a sensation of taste, and cyanide which causes a reflex gasp when it reaches the respiratory centre. Such a method is very limited in its applicability, since there are relatively few substances which do exert a specific and easily recognizable effect at some definite place in the body. In addition, the use of such a method is greatly dependent on the personal response of the subject, and it would not be surprising if quite different results were obtained on carrying out an identical procedure with two different subjects. Errors are also liable to arise owing to the complexity of the system of blood vessels between the site of injection and the place where the response is elicited. The classical methods have recently been adequately reviewed.[82]

The use of radioisotopes offers a solution free from many of the objections cited above. Of the radioisotopes available radiosodium, ^{24}Na, is that normally used in this connexion, and it has the following advantages. As sodium is a normal constituent of blood plasma, the small amount necessary as a tracer can be introduced into the blood without causing any unphysiological response. Its half-life of 15 hr. is long enough for satisfactory experimental observations and yet short enough to minimize the radiation effects which might otherwise be hazardous. Sodium is not selectively absorbed by any tissue, so injected radiosodium will travel in the blood without loss from one site to another. Finally ^{24}Na emits a penetrating γ-radiation which makes it easy to detect through skin and tissue so that external recording is possible.

Many of the studies of blood flow have dealt with its derangement in certain pathological conditions, and some of these will be dealt with below.

In the physiological field, the first studies of blood flow using radiosodium concerned the rate of flow of blood from one arm to the other in young children.[83] The radioactive sodium chloride was injected into one arm, and its appearance in the other arm was detected by means of a Geiger counter placed over the hand. Similar studies have been made[84] by means of a device in which the impulses from the counter, after suitable amplification, were fed to a mechanism operating a pen writing on a kymograph drum. Each impulse caused the pen mechanism to move down one tooth, so that a steady counting rate produced a stepped line of a certain average slope. When the injected isotope arrived at the site over which the counter was placed, the counting rate increased and this was recorded as a change in the slope of the traced line, thus permitting an accurate determination to be made of the time of arrival.

Using this technique with normal human subjects, the average time taken for the blood to flow from the foot to the groin was found to be 18·5 sec., with the subject lying flat on his back and the heel at the same level as the heart. Considerable variation was found from one individual to another and also from one observation to another on the same individual, the range being as much as 7 sec. between two observations carried out on the same subject. The mean rate of flow worked out at 4·45 ± 0·46 cm./sec., and the authors determined the effect of posture on this figure. With the subject seated the rate of flow dropped to 3·03 ± 0·34 cm./sec., while standing erect reduced it still further to 2·62 ± 0·30 cm./sec. As might be expected, lying down 10° from the horizontal with the head lower than the feet gave a higher flow rate, 9·11 ± 0·51 cm./sec., but a still higher value, 9·39 ± 0·44 cm./sec., was found when the subject was lying on his back in a level position as in the standard case, but was made to flex his feet vigorously for 2 min. prior to the injection of ^{24}NaCl. Observations on the flow rate in the arm indicated that it was higher than in the leg, values of the order of 10 cm./sec. being obtained with subjects in the supine position.

Other investigations[85] have extended these observations to a series of pregnant women, and it has been shown that the venous flow rate in the leg diminishes as pregnancy proceeds, returning rapidly to normal after delivery.

A rather specialized application of radiosodium to the study of circulation has been described[86] under the name of radiocardiography. Briefly it involves injecting radioactive sodium chloride into the venous system in such a way that it reaches the right hand chambers of the heart rapidly; from there it goes by the pulmonary circulation to the left side of the heart, and the time interval between the two occasions when the radioisotope reaches the heart is determined using a specially constructed ink-writing Geiger counter placed over the cardiac region. Obstruction to the filling of the right side of the heart is observed as a retardation of the first peak, while any slowing of the pulmonary circulation shows up as a delay in the appearance of the secondary peak. If this second peak fails to diminish at the normal rate, obstruction to the emptying of the left side of the heart is indicated.

The peripheral circulation has been studied in a series of investigations.[87] The method involves a study of the 'build-up curve' of radiosodium in the tissue under study, it being assumed that the rate at which the radiosodium — previously injected elsewhere — builds up in the tissue is directly proportional to the volume of blood flowing through the tissue in unit time. Any derangement of the peripheral vascular system shows up, according to these authors, as a variation from the normal 'build-up curve' and they have claimed that[88] the site of amputation of a limb in, for example, gangrene can be determined by locating the point in the limb where the 'build-up curve' ceases to be normal. They have also used their method to study the effect of a number of drugs used to treat peripheral vascular diseases.[89] Attempts by

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other workers to repeat these observations have not always been successful. Thus, failure to obtain any change in the 'build-up curve' under the influence of drugs, by varying the posture, or during exercise, has been reported.[90] All these conditions are known to vary the flow-rate. The distinction claimed between normal and pathological states has also been denied.[91]

The problem of blood flow in the peripheral circulation has also been studied from the other end, viz. by studying the rate at which the injected radiosodium disappears from the site of injection.[92,93] This method has recently been reviewed.[94] In using this method, it was found that a single exponential function described the disappearance rate. Increased disappearance rates were found in cases of hyperthyroidism and decreased rates in certain peripheral vascular diseases. The difficulty in using this method is that of controlling the factors which can affect the clearance constant. This can be affected by psychological factors such as excitement, and a period of rest for the subject of 10 min. before commencing the experiment has been suggested:[95] other authors[96,97] have recommended periods of rest of up to 1 hr. The question of local trauma, the possibility of a variable degree of leakage back along the needle track and the difficulty of giving the injection always at the same depth and in the same position are variables it is difficult to control. It has also been reported[98] that the clearance constant is greater when the injection is given in a volume of less than 0·02 ml. than when the same amount of radiosodium is contained in a volume of 0·5 to 1·0 ml. The effect of hyaluronidase on the clearance of radiosodium from the subcutaneous tissues in man has been studied[99] and it has been found that it increases the clearance rate. This result is interesting because this enzyme hydrolyzes hyaluronic acid which is sometimes regarded as the substance which cements cells together into tissues. The hydrolysis of hyaluronic acid might therefore be expected to have an effect on the permeability of the capillaries.

An investigation of the role of the lymphatic vessels in the clearance of injected radiosodium from the gastrocnemius muscle of dogs showed that only about 1% of the sodium was cleared by this route, thus supporting the general belief that substances of low molecular weight are cleared from the tissues by the blood stream.[100] A recent study of the clearance method[101] has involved a study of the clearance of radiosodium from the gastrocnemius muscle of human subjects and of the isolated perfused hind limbs of rabbits and cats. The clearance of radiosodium is claimed to be related directly to the blood flow, and not to the capillary surface area. In addition the rate of blood flow appeared to have an effect on the clearance in that there was a lower limit of flow rate below which clearance ceased altogether. On the other hand, with flow rates above the physiological limit, the clearance reached a maximum which could be determined.

The clearance method of studying blood flow in tissues has found considerable application in the field of plastic surgery, where it has been applied to a determination of the normality of blood flow in various types of skin grafts. The subject has been recently reviewed.[102] It is interesting from the general point of view to note that the authors of this review regard one of the uses of the radioisotope technique to be its correlation with various simple clinical tests 'with a view to assessing objectively the value of such tests for routine use under conditions where it is not convenient or practicable to carry out sodium clearance tests.'

Some workers[103,104] have reported differences in the circulation time of blood corpuscles and plasma. It was thought that in the small vessels the corpuscles travelled faster than the plasma, with the net result that the peripheral blood would have a diminished number of corpuscles. This subject has been investigated[105] by injecting into the femoral artery of a cat blood containing ^{32}P-labelled erythrocytes and having $^{42}K_2CO_3$ added to the plasma. Differential counting using a lead filter yielded no evidence for a differential flow.

One clinical problem that has been attacked by the isotope technique using radiosodium is the question of the effect of surgical shock on the capillary permeability. The general trend of the results of such studies indicates that in the tissues subjected to the trauma producing the shock there is an increased permeability of the capillaries and the cell membranes: the capillaries become permeable to protein, and the cell membranes of the fixed tissues become permeable to cations and anions. The rate of removal of radiosodium from the plasma of normal and shocked dogs showed in both groups of animals the same double exponential function.[106] However, in the shocked dogs the rate constant for both phases was reduced to about two thirds of the normal value. Injection of serum or of saline to treat the shock did not restore the rate constants to normal. The authors found that the principal reasons for the reduction of the rate of transfer were the reduction of the plasma volume by about 50% and also the decreased blood flow rate. In another investigation[107] it was calculated that the sodium content of the traumatized tissue was greater than could be accounted for by the accumulation of fluid due to the associated oedema, and it was suggested that the cells of the tissue involved become permeable to sodium and retain this sodium so that it is not available for normal exchange and maintenance of plasma volume. Up to 50% of the normal extracellular phase sodium was estimated to be removed in this way.

RADIATION EFFECTS

Radioactive sodium (^{24}Na) emits radiation of high activity, and this isotope has been used as a radiation source in the treatment of malignant growths. Its use for treatment of carcinoma of the bladder has been described.[108] The solution of ^{24}NaCl was passed into a balloon previously inserted in the bladder, and in this way intracavitary irradiation was carried out.

The radiation from radioactive isotopes constitutes a hazard from the genetic point of view, and some mutation studies on plants with radioisotopes carried out in Sweden have been reviewed.[109] In this work studies were made using ^{22}Na, the long-lived isotope of sodium: barley seeds were soaked in a solution containing the isotope, and the genetic properties of the seeds studied.

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